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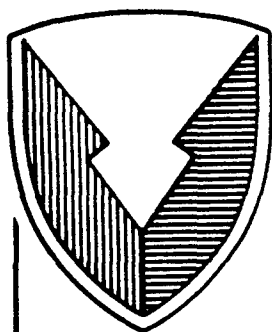
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C E N T E R

Technical Report

No. 13264

CHEMICAL DESIGN OF ELASTOMERS

May 1987

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**U.S. ARMY TANK-AUTOMOTIVE COMMAND
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20020806171

NOTICES

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release: Distribution is Unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION Case Western Reserve University	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION U.S. Army Tank-Automotive Command
6c. ADDRESS (City, State, and ZIP Code) Cleveland, OH 44106		7b. ADDRESS (City, State, and ZIP Code) Warren, MI 48397-5000

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAE07-83-K-R010

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)

Chemical Design of Elastomers

12 PERSONAL AUTHOR(S)
Jack L. Koenig

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 7/1/83 TO 12/30/8	14. DATE OF REPORT (Year, Month, Day) May 19, 1987	15. PAGE COUNT 73

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Tank pads, rubbers, vulcanization, NMR

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Solid state C-13 NMR spectroscopy has been extended to the study of the accelerated sulfur-vulcanization of natural rubber. Natural rubber vulcanizates which had been cured with elemental sulfur only, were studied by this particular technique. The NMR spectra that were obtained for these systems provided significant structural information on the natural rubber network. In this study, the samples are formulated with sulfur, accelerators and activators in order to study the effects of the various components in the crosslinking process of natural rubber. The NMR spectra indicate that a simpler network structure is obtained with accelerated sulfur vulcanization as compared to the systems cured with high levels of elemental sulfur. Solution C-13 NMR model compound studies have indicated that polysulfides terminated by accelerator residues will be indistinguishable from polysulfidic crosslinks. In the natural rubber vulcanizates, polysulfidic crosslinks have been observed in addition to the pendant accelerator groups. Cis-to-trans chain isomerization has been found to occur in these vulcanizates.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Jack Patt	22b TELEPHONE (Include Area Code) 313/574-8687	22c. OFFICE SYMBOL AMSTA-RTT

DD FORM 1473, 84 MAR
83 APR edition may be used until exhausted.
All other editions are obsolete.

TABLE OF CONTENTS

1.0. INTRODUCTION

This final technical report, prepared by Case Western
Reserve University for the U.S. Army Tank-Automotive
Command (TACOM) under contract #DAAE07-83 K-R010, describes
the results of Nuclear Magnetic Resonance (NMR) studies
on the structure of vulcanized rubber. This work was
initiated in order to generate improved tank pads for
the Army.

2.0. OBJECTIVE

The primary goal was to improve the rubber materials
used in tank pads yielding greater resistance to shear
and fatigue failure.

3.0. CONCLUSIONS

The NMR approach allows, for the first time, the identification
of the chemical structure of crosslinks generated by
sulfur-accelerated vulcanization. Further work will
reveal the crosslinks which are susceptible to shear
and fatigue failure. With this knowledge, improved rubbers
for tank pad applications can be designed based on modification
of the vulcanization process.

4.0. RECOMMENDATIONS

4.1. Rubber Analysis

This work has revealed that high-resolution NMR is a
viable technique for analysis of the network structure
of rubber. Further work with the new technique of NMR
imaging will allow a scan of the damaged portion which
will demonstrate the chemical mechanism of failure.

4.2. Vulcanization Process

This work has demonstrated that the networks generated
by accelerated sulfur-vulcanization yield a simpler crosslink
structure which should be reflected in the properties.
Further examination of accelerated vulcanization is recommended.

4.3. Tank Pads

It is recommended that network structure determinations
be made using NMR on tank pads under their use conditions
and after failure to determine the chemical basis of
the initiation of the failure.

5.0. DISCUSSION

5.1. General

Sulfur vulcanization of natural rubber has been studied for many years by many researchers since the initial discoveries of Charles Goodyear and Thomas Hancock. A variety of techniques including chemical, physical and mechanical, have been used to characterize the rubber network (1,2). Some of the effort has been driven to develop improved properties and generate further applications of these vulcanizate systems. The compounds and additives used in the processing of the natural rubber vulcanizates have been changed through the years in order to obtain specific material properties which comply with final use conditions. Years of research on the natural rubber crosslinking chemistry and network structure has yielded a reasonably well-accepted reaction mechanism of sulfur vulcanization and insights into the final network structure (3-7). One of the primary approaches has involved the study of model compounds. The model compounds are reacted with sulfur and the other various components of the vulcanization process, in a manner similar to the curing of natural rubber Other research methods have included a chemical probe analysis of the vulcanizates. This approach provides information on the amounts of mono, di and polysulfidic crosslinks that are generated with a particular curing formulation.

In the field of polymer science, Carbon-13 (C-13) (NMR) spectroscopy has proven to be a powerful method for molecular structure elucidation. The C-13 NMR method has been used to identify elastomers and to determine structural features such as monomer sequence distribution, comonomer composition and stereospecific structure (8-10). Cured, filled elastomeric compounds have been analyzed for unknown components using solution C-13 NMR methods (11). Recently, the C-13 (MAS) technique has been used together with the standard Bloch decay experiment to study vulcanizates (12). The elastomeric components of filled vulcanizates were quantitatively characterized in their solid state, without the need for special sample preparation. In another recent study, the solid state C-13 NMR techniques have been used in addition to the Bloch decay experiments, in order to follow the peroxide curing of both natural rubber and polybutadiene (13). This work illustrated the usefulness of different pulse sequences for NMR experiments on elastomeric systems that are highly crosslinked.

Solid state C-13 NMR spectroscopy has proven to be very useful for structure studies particularly on polymeric systems (14-16). This success has prompted the use of these NMR techniques for the characterization of peroxide and sulfur-vulcanized natural rubber systems. In these

studies, MAS and high-power proton decoupling have been used both with and without cross polarization (CP) to produce high-resolution C-13 NMR spectra of sulfur-crosslinked natural rubber samples.

The intent of this research was to obtain a further understanding of the final vulcanizate network structure and any insights into the mechanism of vulcanization. The extensive model compound data found in the literature indicates several different positions for sulfur attachment to the natural rubber chain. It has also been determined that the crosslinks have variations in sulfur rank. Other main chain modifications have also been observed. In this part of the investigation, natural rubber systems vulcanized with only elemental sulfur have been studied. With the aid of the appropriate pulse sequences in the C-13 NMR experiments, it is possible to study the formulated natural rubber samples. The data is analyzed for evidence of crosslink formation and any main chain structural modifications that occur during the curing process. Some of the structural features that are generally accepted as occurring in these systems are shown in Figure 5-1. The structures include cyclic sulfides, pendant accelerator groups and cis-to-trans isomerization, in addition to the different crosslink types.

A series of model compounds for sulfur-vulcanized natural rubber have also been studied by C-13 NMR spectroscopy. The materials were obtained from Dr. M. Porter of the Malaysian Rubber Producers Research Association (MRPRA). The model compounds are based on 2-methyl-2-pentene which has been selectively sulfurated. This particular alkene models the a-methylic site and one of the two a-methylenic sites of polyisoprene (17). The model compounds that have been obtained and studied are illustrated in Figure 5-2. These systems model the mono, di and trisulfidic crosslinks of sulfur-vulcanized natural rubber. The C-13 solution NMR spectra were obtained for these model compounds in order to aid in the NMR peak assignments of the sulfur-vulcanized natural rubber spectra. The motivation was to find chemical shift trends for the model systems which could then be applied to the spectroscopic results of the vulcanized materials.

5.2. Experimental

The solution C-13 NMR spectra for these model compounds were obtained on a Varian XL-200 NMR spectrometer. A spectral width of 12,000 (Hz) and 8 K data points were used for the data collection. A 15 microsecond pulse width was utilized with a 1.3-second acquisition time. 64 to 128 scans were typically taken for each sample. The chemical shifts were determined for these compounds which were in $(CDCl_3)$ solutions, in (ppm) from internally added tetramethylsilane (TMS).

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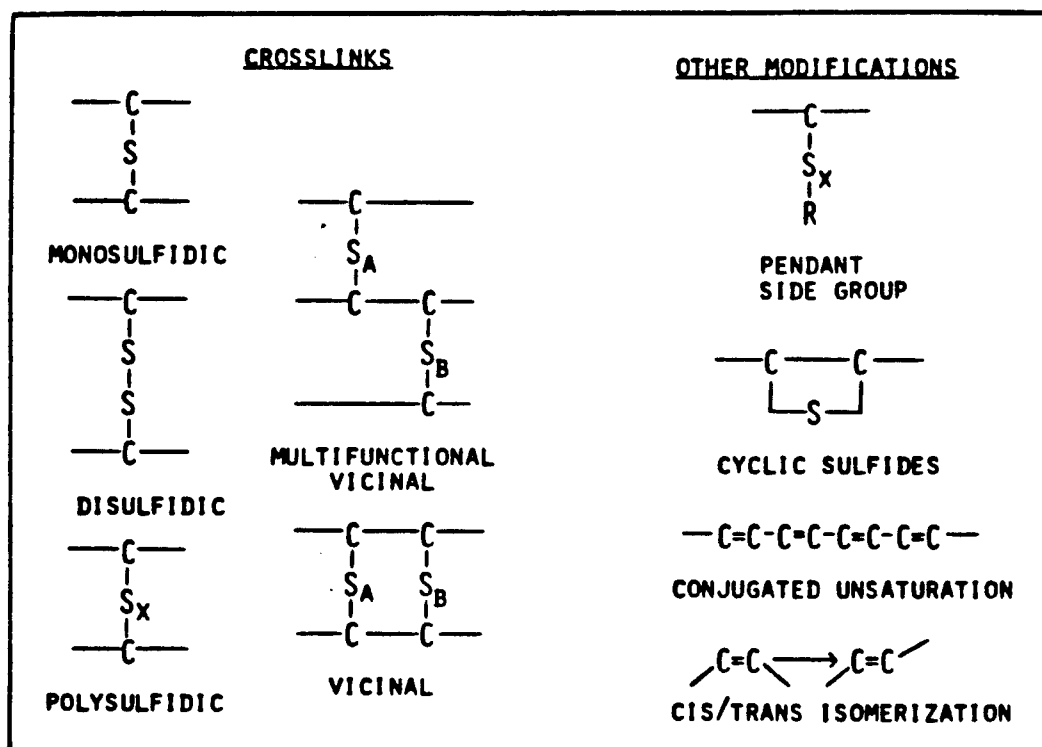# SOME STRUCTURAL FEATURES OF SULFUR VULCANIZED RUBBERS

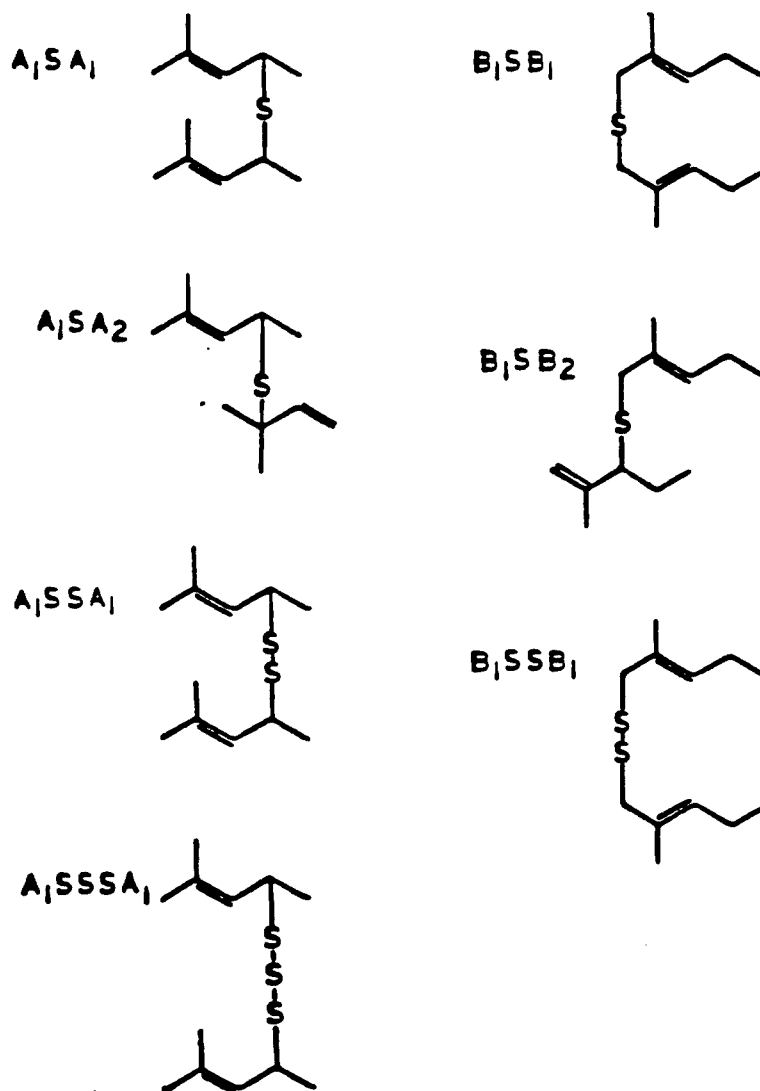Figure 1. Structural features of sulfur vulcanized natural rubber

Figure 2. Compounds based on 2-methyl-2-pentene and studied as
models for sulfur vulcanized natural rubber

The natural rubber used in the vulcanized formulations has the technical classification SMR-5. The natural rubber samples with various amounts of elemental sulfur were mixed together in a Brabender mixer head. The temperature of the mixer head was maintained at 70 ^{o}C for 30 minutes. The samples were cured using a template in a temperature-controlled hydraulic press with a pressure of 2,000 (psi). The curing temperatures were 140 ^{o}C and 150 ^{o}C for various lengths of time which are specified in the text.

Equilibrium swelling measurements were carried out for all the samples. Rubber vulcanizate samples weighing approximately 0.2 grams were swollen in benzene until the diffusion equilibrium was reached (18). The samples were weighed before the swelling and then in the swollen state to determine the swell ratio. The swell ratio is defined as: $R=(W^t-W^o)/W^o$ where W^o is the weight of the test piece before swelling and W^t is the weight of the swollen test piece after time t of immersion. The swell ratio measurements indicate the degree of crosslinking in the system, therefore the smaller the ratio, the higher the degree of crosslinking on a relative basis.

The C-13 NMR studies were performed at 37.7 (MHz) on a modified Nicolet NT-150 spectrometer. MAS was used to obtain all the spectra. A variable temperature probe obtained from Doty Scientific was used in the NMR experiments (19). Cylindrical NMR sample spinners made of Al_2O_3 were utilized. The vulcanizate samples were rolled and fit into the spinners which then typically spun between 2.5 to 3.0 (kHz). Figure 5-3 is a schematic representation of the two different pulse sequences used in the C-13 NMR studies. The gated high-power decoupling (GHPD) pulse sequence is used for systems having sufficient chain mobility. A 90-degree carbon pulse is applied in the GHPD experiment followed by high-power proton decoupling in order to observe systems which have strong dipolar coupled carbons and protons but are still sufficiently mobile. Gated decoupling was used so that the spectra, which are acquired as Bloch decays, are obtained without an (NOE) (20). The delay between pulse sequence repetitions for this NMR experiment was 5 seconds. Each GHPD spectrum is the average of 3,000 transients. Cross polarization (21) discriminates heavily against mobile regions, therefore, the (CP) pulse sequence which is represented in Figure 5-3(b) is utilized for the rigid and semi-rigid systems. In this experiment the proton nuclei receive the initial 90-degree pulse. Then the magnetization is transferred from the protons to the carbons after which the acquisition occurs. The Hartmann-Hahn condition for CP was adjusted for radiofrequency field strengths between 50-75 kHz (22). The carbon-proton contact time was 1 millisecond and the delay between successive pulses was 2 seconds. 8,000 transients were typically collected for the CP spectra.

PULSE SEQUENCES

GATED HIGH POWER DECOUPLING EXPERIMENT
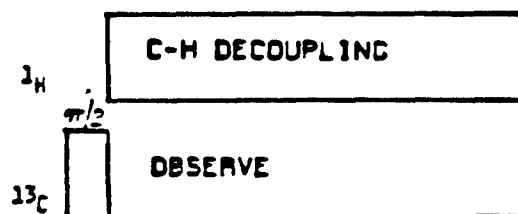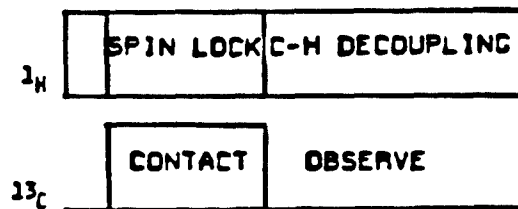

CROSS POLARIZATION EXPERIMENT

Figure 3. Pulse sequences for (A) the gated high-power decoupling experiment (GHPD) and (B) the cross-polarization experiment (CP).

All chemical shifts are reported in ppm with respect to TMS.

5.2.1. Chemical Shift Calculations. Chemical shifts have been calculated using additivity rules for some of the structural features that may form during sulfur vulcanization. The calculations for the sulfur crosslink positions were carried out using the shielding parameters found in Table 5-1. The aliphatic additivity constants for the various sulfur groups were obtained from "The Sadtler Guide to Carbon-13 NMR Spectra" (23). The sulfur shielding values were added to the initial chemical shift

Table 5-1. Aliphatic Additivity Constants

(Sadtler C-13 NMR Index)

HS-	C1=+10.5	C2=+11.4	C3=-3.6	C4=-0.2
CH3-S-	C1=+20.4	C2= +6.2	C3=-2.7	C4=+0.3
R-S-S-	C1=+25.2	C2= +6.6	C3=-3.4	C4=-0.1
R-S-	C1=+17.9	C2= +7.1	C3=-3.0	C4=-0.1

values of the cis-1,4-polyisoprene carbons to determine the chemical shifts for the sulfurated species. The crosslinking reaction may result in a saturated system, the starting chemical shift values of a section of the ethylene-propylene copolymer were used (24). The chemical shift data for the initial structures can be found in Table 5-2 and the calculated chemical shifts for the sulfurated natural rubber systems are tabulated in Table 5-4. These calculations were also carried out for the model compounds using literature values for the starting C-13 chemical shifts of the appropriate alkenes (25,26). The results are listed in Table 5-3.

Sulfur-induced vulcanization will also lead to the formation of cyclic sulfides as has been shown with the model compound studies of the past. Cyclic sulfides should be observed in these natural rubber vulcanizates. The previous studies showed that both five- and six-membered cyclic rings containing one sulfur atom may be formed. The structures of these cyclic sulfides are shown in Figure 5-4. Chemical shift calculations were carried out for these cyclic structures. The parameters used for this calculation were obtained from the literature (27). In addition, the C-13 NMR chemical shifts for several model cyclic sulfides found in the literature are also given in Figure 5-4 (28-30).

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Table 5-2. Chemical Shift Data

Cis-1,4-polyisoprene

       5 CH3

    -CH2-C=CH-CH2-
      3   1 2   4

```
1 - 134.8 ppm
2 - 125.3
3 -  32.5
4 -  26.7
5 -  23.6
```


Ethylene-propylene segment

        6 CH3

-CH2-CH2-CH-CH2-CH2-
  1   2   3   4   5

```
1 -  27.6 ppm
2 -  37.5
3 -  33.1
4 -  37.5
5 -  27.6
6 -  20.1
```


2-methyl-2-pentene

   6 CH3

CH3-C=CH-CH2-CH3
1   2 3   4   5

```
1 -  25.7 ppm
2 - 130.6
3 - 126.9
4 -  21.5
5 -  14.5
6 -  17.5
```


2-methyl-1-pentene

   6 CH3

CH2=C-CH2-CH2-CH3
1   2 3   4   5

```
1 - 110.0 ppm
2 - 145.8
3 -  40.3
4 -  21.0
5 -  13.8
6 -  22.4
```


4-methyl-2-pentene

        5 CH3

CH3-CH=CH-CH2-CH3
1   2 3   4   5

```
1 -  12.3 ppm
2 - 138.6
3 - 121.3
4 -  26.4
5 -  22.9
```

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CALCULATED CHEMICAL SHIFTS (PPM) FOR CYCLIC SULFIDE STRUCTURES
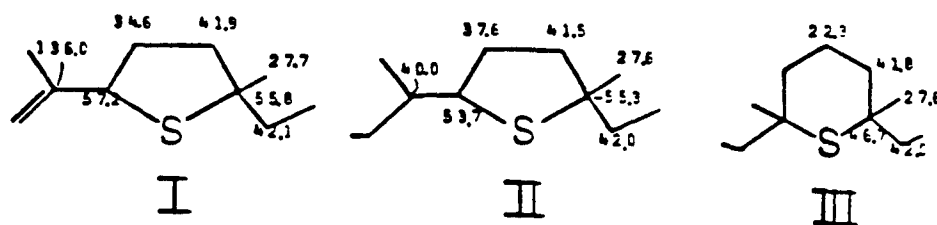
COMMON CYCLIC SULFIDES WITH CHEMICAL SHIFTS (PPM)

Figure 4. Cyclic sulfide structures and calculated chemical shifts. Model cyclic sulfides and chemical shifts taken from the literature (references 28-30)

15
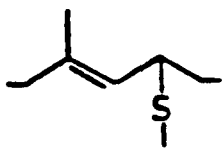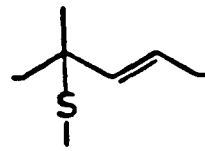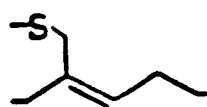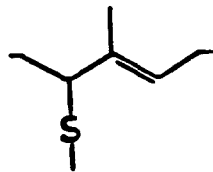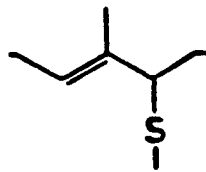
Table 5-3. Observed and Calculated Chemical Shifts (PPM)

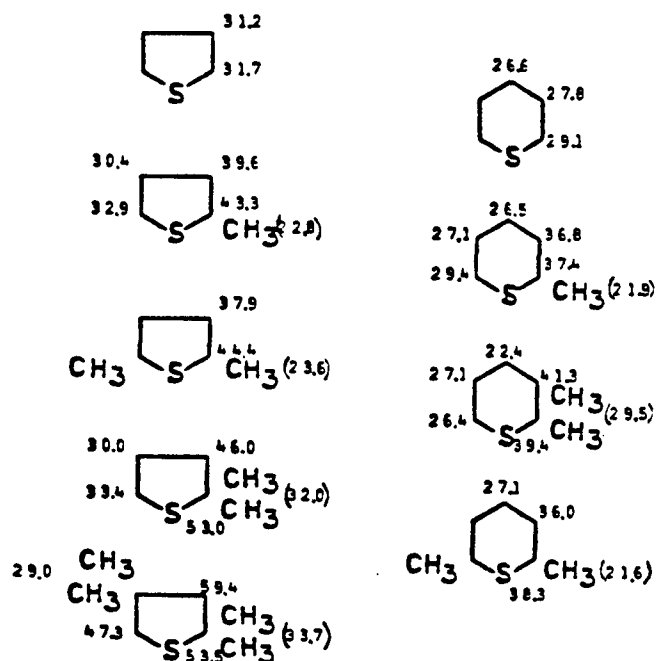| Model Compound	C-S bond	Observed Chemical Shift	Calculated Chemical Shift
A_1SA_1	HC-S-	36.8 ppm	21.5+17.9=39.4
A_1SA_2	HC-S-	36.8 ppm	21.5+17.9=39.4
	H_3C-C-S-	47.1 ppm	26.4+17.9=44.3
A_1SSA_1	HC-S-S-	43.6;44.0 ppm	21.5+25.2=46.7
A_1SSSA_1	HC-S-S-S-	44.1 ppm	21.5+25.2=46.7
B_1SB_1	H_2C-S-	40.0 ppm	25.7+17.9=43.6
B_1SSB_1	H_2C-S-S-	48.9 ppm	25.7+25.2=50.9
B_1SB_2	H_2C-S-	40.0;40.4 ppm	25.7+17.9=43.6
	HC-S-	53.2;54.7 ppm	40.3+17.9=58.2

Other main chain modifications are also expected to occur in the network structure including cis-to-trans chain isomerization and conjugated unsaturation. These changes are easily detected.

5.2.2. Model Compounds. The observed chemical shift values for the resonance peaks corresponding to the carbon groups of the model compounds which are involved in the various sulfur linkages are tabulated in Table 5-3. In the comparison of the calculated to the observed chemical shifts for these model compounds, it is apparent that the calculated values are higher than the observed values in all but one case. These results reflect expected limitations in the shielding parameters. The substituent parameters are derived from a large volume of NMR data for sulfurated compounds and are, therefore, average values obtained from all the components. Nagata, et al., measured the C-13 NMR chemical shifts for a small group of thiols, sulfides and disulfides and studied the behavior of the chemical shifts for the a-carbons and b-carbons in these compounds (31). The researchers found that the chemical shifts of the a-carbons are gradually shifted to lower fields in the order of methyl, methylene, methine and quaternary carbons. The chemical shifts of the a-carbons are shifted to lower fields in the order of thiols, sulfides and disulfides, while the order is reversed for the β-parameters of Table 5-1 should be adjusted when added

Table 5-4.   Calculated Chemical Shifts for Monosulfidic and
            Polysulfidic Crosslinks (PPM)

Possible Structures		Mono	Di(Poly)
A	1	26.7+17.9=44.6	+25.2=51.9
	2	32.5+7.1=39.6	+6.6=39.6
	3	125.3+7.1=132.4	+6.6=132.4
B	1	33.1+17.9=51.0	+25.2=58.3
	2	20.1+7.1=27.2	+6.6=26.7
	3	130+7.1=137.1	+6.6=136.4
	4	37.5+7.1=44.6	+6.6=44.1
C	1	23.6+17.9=41.5	+25.2=48.8
	2	134.8+7.1=141.9	+6.6=141.4
D	1	32.5+17.9=50.4	+25.2=57.7
	2	134.8+7.1=141.9	+6.6=141.4
	3	26.7+7.1=33.8	+6.6=33.3
E	1	37.5+17.9=55.4	+25.2=62.7
	2	27.6+7.1=34.7	+6.6=34.2
	3	134.8+7.1=141.9	+6.6=141.4

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to the different types of carbon groups. For example, a methylene group would have a slightly lower shielding value than a methine group. But another consideration is the case of the sulfurated quaternary carbon of A^1SA^2, which is observed at a higher chemical shift position than the calculated value. Steric effects which may be associated with the specific configuration of the bond may be contributing to the chemical shift for this particular carbon (32). This information will be important for the calculations and considerations of the chemical shifts obtained for the sulfur-vulcanized natural rubber systems.

The observed chemical shift data obtained from the model compounds indicate several important trends which may be extended to the C-13 NMR data of sulfur-vulcanized natural rubber. First it is interesting to note that the chemical shift difference between the disulfidic link and the monosulfidic link for the A^1S-type system in which a methine carbon group (-CH-) is involved in the bonding lies between 6.8 to 7.2 ppm. For the B^1S-type system in which a methylene carbon group ($-CH^2-$) is bonded leading to a disulfidic or a monosulfidic link, this difference is slightly higher at 8.9 ppm. The shielding parameter values have a difference of 7.3 ppm between the disulfidic and the monosulfidic substituent groups. This data indicates that monosulfidic and disulfidic crosslinks should be distinguishable in the C-13 NMR spectra of sulfur-vulcanized natural rubber. For attachment to a particular carbon, monosulfides should be distinquishable from disulfides by 7 ppm or more.

One trisulfidic model compound, A^1SSSA^1, was studied. The chemical shift of the methine carbon for this case was observed at 44.1 ppm. The analogous disulfidic model system, A^1SSA^1, had a methine carbon chemical shift at virtually the same chemical shift position in the C-13 NMR spectrum. These results indicate that it may not be possible to distinquish disulfidic crosslinks from crosslinks of higher sulfur rank. From the chemical shift point of view, a polysulfidic link may be a crosslink containing two or more sulfur atoms. In their work on the characterization of elastomers and rubber chemicals using NMR, Komoroski et al. (33) have also shown that monosulfidic crosslinks should be resolved from disulfidic crosslinks. Their studies on model sulfidic compounds have shown that the chemical shift differences for a carbon bonded to a disulfide versus a trisulfide are on the order of 1 ppm at most. The data verify that at this level of NMR resolution, disulfidic and polysulfidic crosslinks will probably not be resolvable from each other.

5.2.3. Sulfur Vulcanized Natural Rubber. The C-13 solid state NMR spectra of both the cis and the trans forms of 1,4-polyisoprene obtained by the GHPD pulse sequence are shown in Figure 5-5. In both cases five distinct
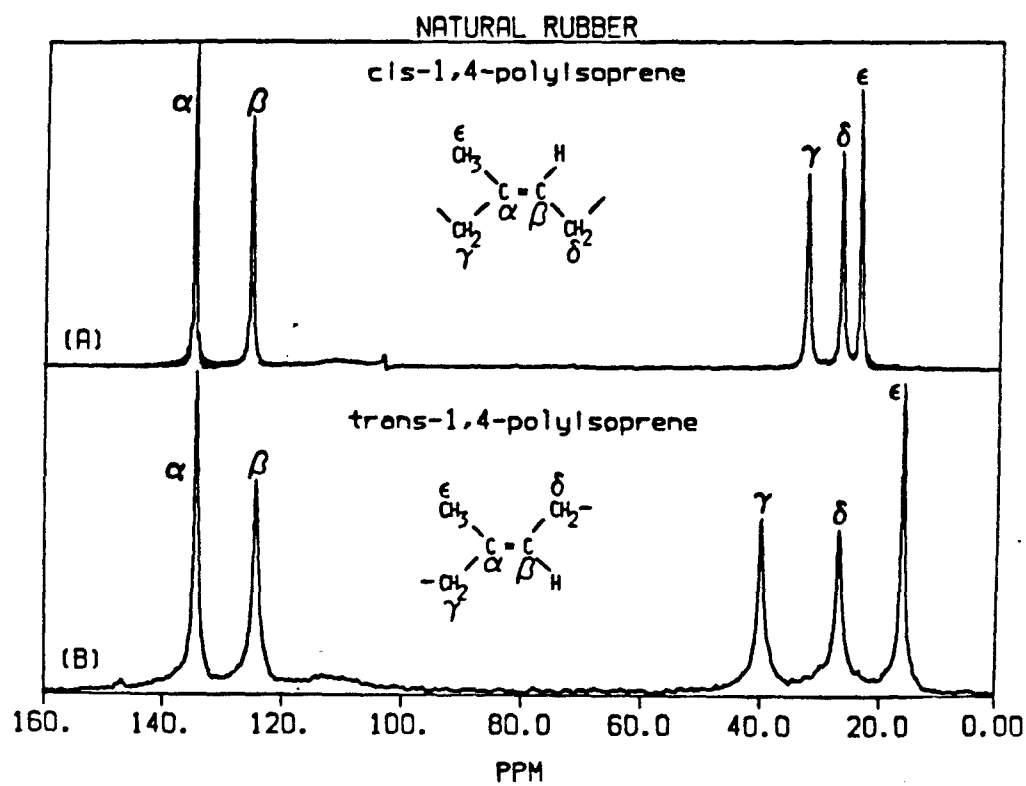
Figure 5. The C-13 GHPD/MAS NMR spectra of (A) cis-1,4-polyisoprene and (B) trans-1,4-polyisoprene

resonances appear for the five different carbon groups
present in the repeat structure of the 1,4-polyisoprenes.
The common form of natural rubber is the cis isomer with
resonances appearing at 134.8, 125.3, 32.5, 26.7 and 23.6
ppm. The trans isomer has resonance peaks appearing at
134.4, 124.4, 39.9, 26.9 and 16.0 ppm. The peaks are
labeled on the spectra. The assignments have been
documented in the past (34,35).

The C-13 GHPD/MAS NMR spectra obtained for natural rubber
mixed and cured with 10% sulfur by weight, are shown in
Figure 5-6. The curing time ranged from 10 to 90 minutes
at 150 °C. The most obvious change in the spectra is the
increased linewidth with cure time. The changes in
half-width of the natural rubber resonances are tabulated
in Table 5-5. The five resonances due to the unaltered
natural rubber carbons are prominent especially initially.
After 10 minutes of. cure, new resonances are observed at
57.5, 50.2, 44.6, 40.1, 30.0, 18.0, 16.1 and 14.0 ppm. The
same resonances are observed in the spectrum of the
15-minute cured sample. For longer curing times, the
aliphatic carbon region between 10 and 60 ppm becomes broad
with a loss of spectral resolution. Broadening is also
observed in the olefinic region of the spectra. At all the
degrees of cure a prominent resonance is observed at 58 ppm
in the C-13 NMR spectra. If natural rubber is cured with
10% sulfur for 9 hours at 140°C, the resulting GHPD/MAS NMR
spectrum closely resembles the spectra found in Figures
5-6(c) through 5-6(f).

Table 5-5.   Half-width of Natural Rubber Resonances Obtained
             by Lorentzian Curve-Fitting (PPM)

| | 134.8ppm | 125.3ppm | 32.5ppm | 26.7ppm | 23.6ppm |
	-C=	=CH-	-CH2-	-CH2-	-CH3
NR	0.19	0.23	0.29	0.27	0.20
5 min	0.26	0.34	0.44	0.39	0.27
10 min	0.25	0.38	0.52	0.45	0.26
15 min	0.31	0.56	0.82	0.62	0.35
30 min	0.50	0.89	0.95	0.68	0.46
45 min	0.48	0.91	1.01	0.66	0.46
60 min	0.50	1.04	0.93	0.62	0.48
90 min	0.56	1.18	0.80	0.59	0.54

The swell ratios for the sulfur-vulcanized natural rubber
samples of Figure 5-6 are plotted against their
corresponding cure times, in the top plot of Figure 5-7.
The data in the middle plot of Figure 5-7 represent the
intensity behavior of the resonance peak found at 58 ppm in
the NMR spectra obtained for the same samples. The middle
set of data points were obtained by taking the ratio of
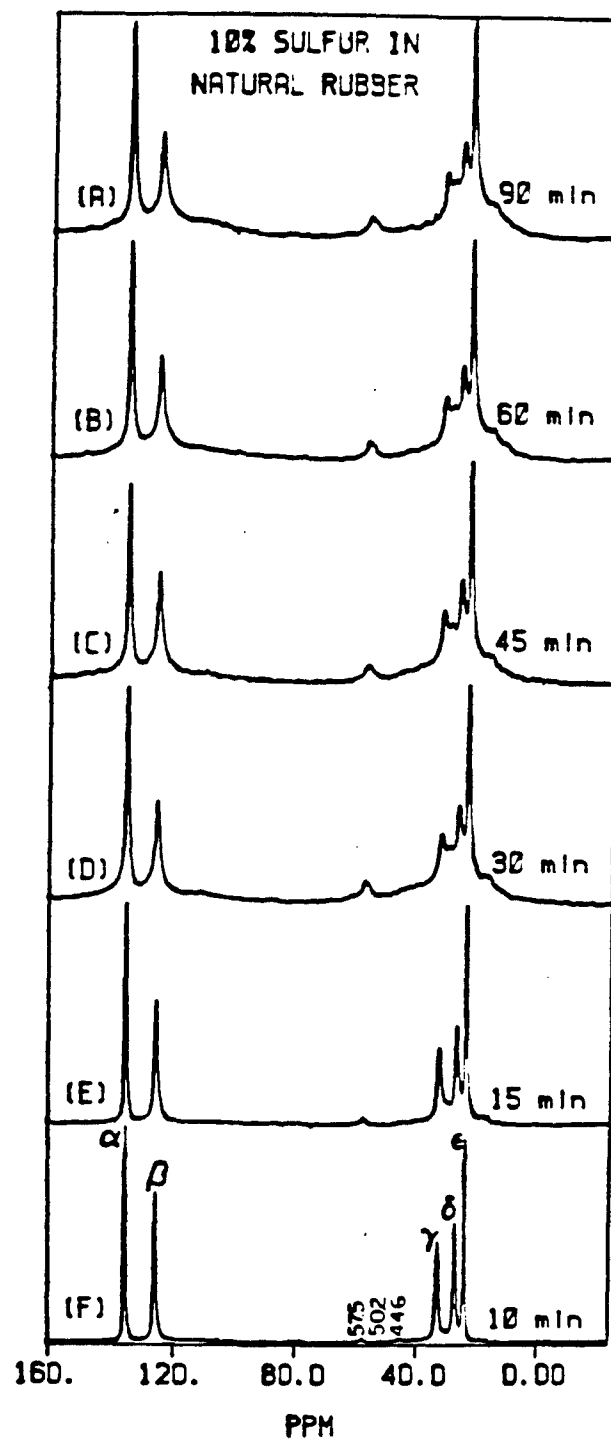
Figure 6. The C-13 GHPD/MAS NMR spectra of natural rubber cured with 10% sulfur at 150°C for times ranging between 10 and 90 minutes

21
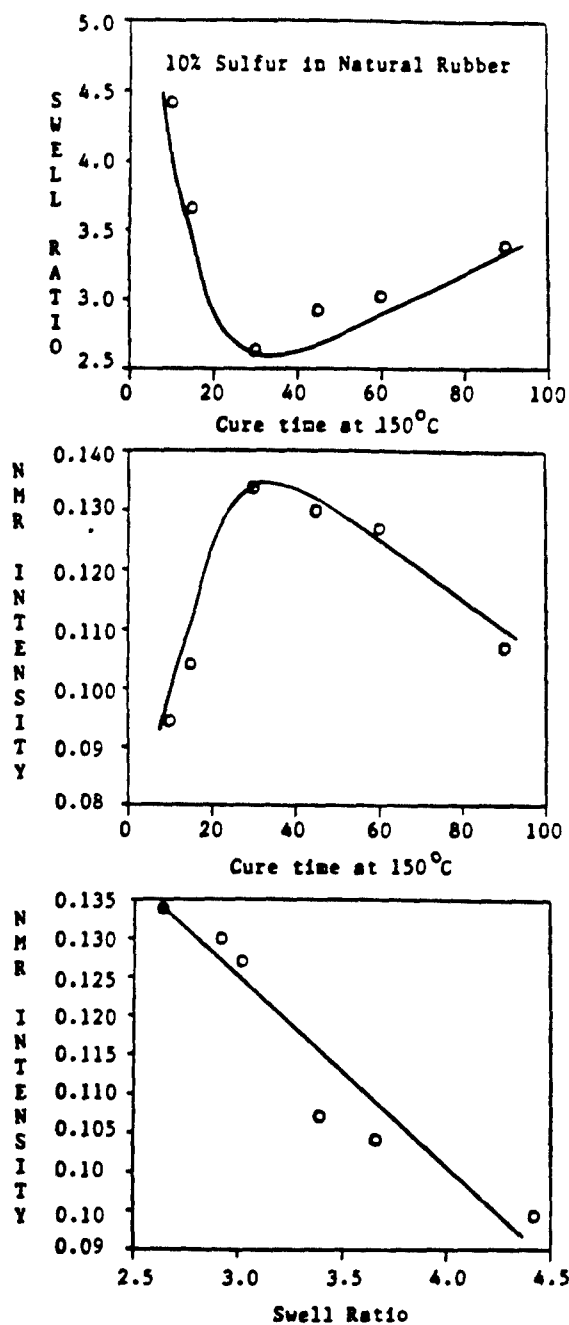
Figure 7. (A) Swell ratio plotted vs cure time for 10% sulfur-cured
natural rubber samples in the spectra of Fig. 6. (B)
ratio of intensities for peaks appearing at 50 ppm (a new
resonance) to 23.6 ppm (resonance due to the methyl carbons
of natural rubber) vs cure time, (c) the NMR intensity at
58 ppm is plotted against swell ratio

intensities for the peak appearing at 58 ppm with respect to the peak at 23.6 ppm. The resonance observed at 58 ppm arose with the curing process, while the peak at 23.6 ppm is due to the methyl carbons of natural rubber. For this set of vulcanized natural rubber samples, the swell ratio decreases for the samples cured to 30 minutes after which there is a slight increase in swell ratio. The intensity ratio data exhibit the reverse behavior. These data increase up to 30 minutes of cure at 150 ^{o}C, and then decrease. In the bottom plot of Figure 5-7, the NMR intensity is plotted against the swell ratios of these natural rubber samples cured with 10% sulfur. The relationship between the two is linear indicating that the resonance at 58 ppm is associated with a crosslink structure.

The cross polarization NMR spectra have also been obtained for all the 10% sulfur-cured natural rubber samples. The C-13 CP/MAS spectra are plotted for the samples cured at 150 ^{o}C for 15, 30 and 60 minutes in Figure 5-8. As opposed to the GHPD experiment which is especially sensitive to the mobile portions (uncrosslinked or lightly crosslinked) of the samples, the CP NMR experiment is measuring the spectra of the more rigid or highly crosslinked portion of the network. In the CP spectrum of the sample cured for 15 minutes, only the peaks due to the natural rubber carbons are observed, but with considerable broadening. The resonances in the spectra of the 30- and 60-minute cured samples are further broadened and overlapped in all the spectral regions. A portion of the natural rubber must be immobilized by the crosslinking process in order to observe the peaks with the CP pulse sequence. New resonances are observed at approximately 58, 64, 73 and 81 ppm in the spectra of Figures 5-8(a) and 5-8(b). In the corresponding GHPD/MAS NMR spectra which are found in Figure 5-6, the only pronounced new resonance is observed at 58 ppm. Generally the cross polarization spectra obtained for this series of vulcanized samples have a lower signal-to-noise ratio than the gated high-power decoupling spectra in-spite of the proton enhanced nature of the CP spectra. The lower signal-to-noise ratios of the CP spectra indicate that only a small portion of the sample is highly crosslinked.

Natural rubber was also cured with 20% and 30% by weight elemental sulfur. Figure 5-9 shows both the GHPD and CP/MAS NMR spectra of natural rubber cured with 30% sulfur at 150 ^{o}C for 60 minutes. This particular formulation also contained 5 parts zinc oxide, 1 part antioxidant and 2.5 parts stearic acid. In this case the CP spectrum is very similar to the GHPD spectrum. A prominent new resonance appears at approximately 58 ppm in both spectra. The broad resonances are heavily overlapped in all of the spectral regions.

5.2.4. Resolution Enhancement Through Increased Mobility.

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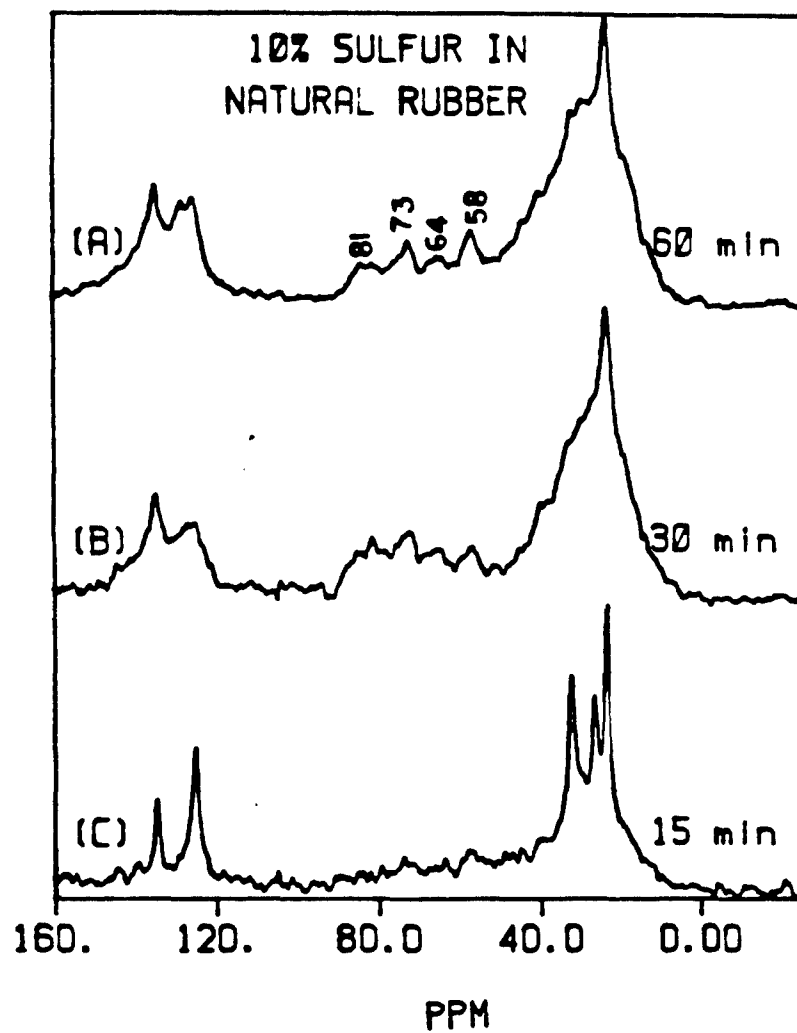
Figure 8. The C-13 CP/MAS NMR spectra of natural rubber cured with 10% sulfur at 150°C for 15, 30 and 60 minutes. Observe the increased line broadening with cure time
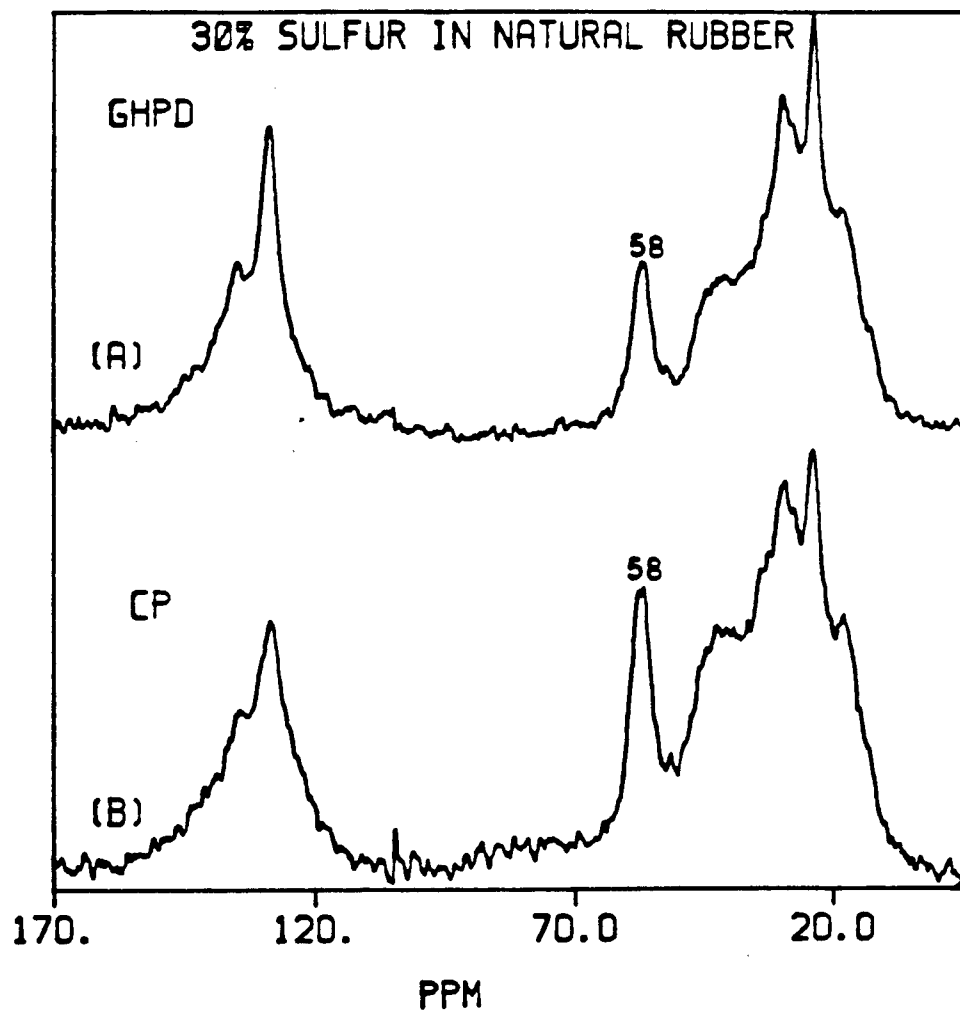
Figure 9. The C-13 MAS NMR spectra of natural rubber cured with 30% sulfur, 5 parts zinc oxide, 1 part antioxidant and 2.5 parts stearic acid, at 150°C for 60 mins. (A) GHPD spectrum and (B) CP spectrum. The similarity of these spectra indicates that the network structure of the rigid and mobile regions of the vulcanized rubber are very similar

Increased spectral resolution was desired for these highly cured natural rubber vulcanizates. Using a variable-temperature NMR probe, it is possible to raise the temperature of the samples. The idea was to induce some degree of mobility in the samples by this method. The increased mobility should lead to narrower resonance lines. The resulting C-13 GHPD/MAS NMR spectrum measured at 80 ^{o}C for the natural rubber cured for 60 minutes with 10% sulfur is shown in Figure 5-10(b). The spectrum in Figure 5-10(c) is of the same sample obtained at room temperature. The resonance peaks measured at 80 ^{o}C of the natural rubber chain are now much sharper and prominent. It is possible to distinguish the resonances which arose during the vulcanization process after 30 minutes of curing. The peak which previously appeared at roughly 58 ppm is split into two peaks. The chemical shift positions of all the new resonances are: 57.5, 56.5, 44.6, a shoulder at 43.0, 40.1, 38.6, 36.1, 30.0, 18.0, 16.1 and 14.0 ppm. The same type of enhanced resolution effect can also be achieved by swelling the vulcanizate samples in an appropriate solvent. The NMR spectrum of the swollen sample is then subsequently obtained at room temperature. Under the same variable-temperature-probe conditions for the 30-minute cured sample, an additional small resonance is observed at 50.2 ppm. This particular resonance is only observed for the 10% sulfur systems cured up to 30 minutes. The NMR spectrum taken at 80 ^{o}C of the natural rubber sample cured for 90 minutes is essentially the same as the spectrum of the 60-minute sample.

The samples of 20% and 30% sulfur-cured natural rubber were also run at higher temperature using the variable-temperature NMR probe. The induced mobility in the sample resulted in enhanced spectral resolution. The C-13 GHPD/MAS NMR spectra for these two systems are shown in Figure 5-11, together with the 10% vulcanized sulfur system. All three samples were cured at 150 ^{o}C for 60 minutes. Generally, the same resolved resonances appear for all three crosslinked systems with some variations in intensities. The new peaks for the 20% sulfur-cured sample are the same as in the 10% sulfur-cured sample except that a shoulder is also observed at approximately 55 ppm. The increase in sample measurement temperature has also provided more spectral resolution for the 30% sulfur-cured system. The resonances which appear in the 10% and 20% sulfur systems also appear in the spectrum of Figure 5-11(c) for the 30% system. Two additional resonances are observed at 33.4 and 25.2 ppm.

5.2.5. Spectral Changes Induced by Cure Time and Sulfur Composition. Raising the measurement temperature of the vulcanized samples that had broad NMR spectra at room temperature, provided a means for obtaining NMR spectra with additional structural information. Quantitative information was desired for these vulcanizates using the

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10% SULFUR IN NR
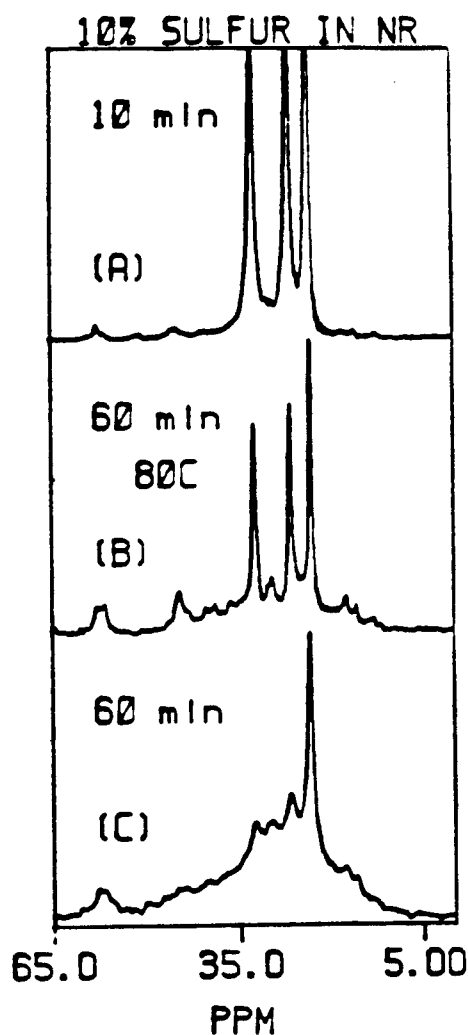
Figure 10. The C-13 GHPD/MAS NMR spectra of natural rubber cured with 10% sulfur at 150°C. (A) spectrum of 10 min cured sample (same spectrum as in Fig. 6(f). (B) spectrum of sample cured for 60 mins with measurement temperature at 80°C using the variable temperature probe. (C) spectrum of same sample as in (B) at room temperature measurement. Observe that the higher NMR measurement temperature yields higher resolution and more resonance lines are observed

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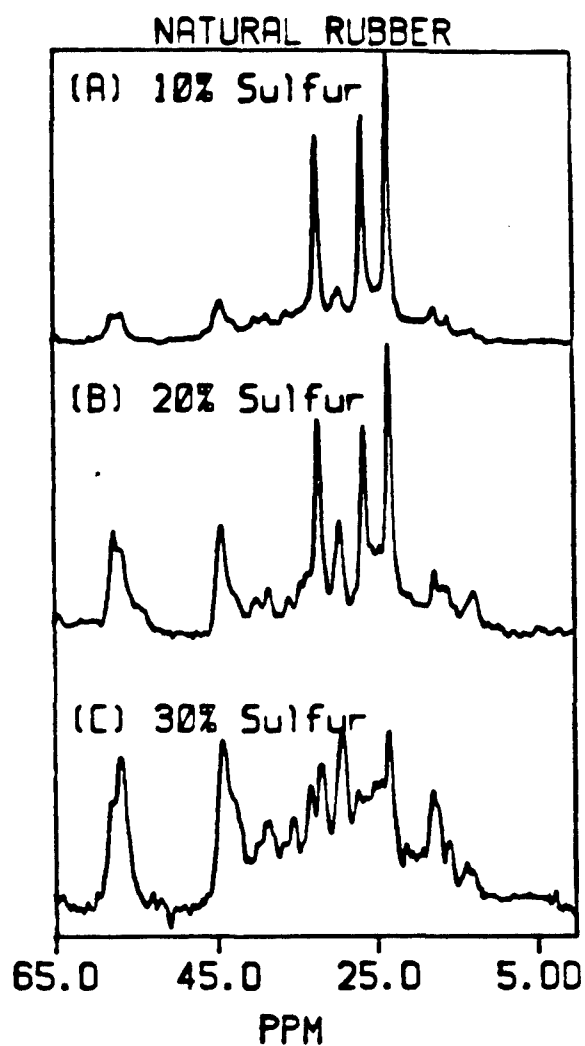
Figure 11. The C-13 GHPD/MAS NMR spectra of natural rubber cured with sulfur for 60 mins at 150°C and the measurement temperature at 80°C. (A) 10% sulfur (B) 20% sulfur and (C) 30% sulfur by weight in the formulation

NMR spectra. Semi-quantitative NMR measurements have been obtained with consideration of the NOE and the C-13 T1 effects Peak areas were determined for a series of the sulfur-cured natural rubber spectra. This was done both by curve-fitting the experimental spectra with Lorentzian line shapes and by absolute peak area determination. Theoretically, NMR peak shapes are Lorentzian (36). The peak area data determined by Lorentzian curve-fitting provided more accurate results than the absolute peak areas because of the considerable overlap in the NMR spectra of the vulcanizates. In Figure 5-12(a), the C-13 GHPD/MAS NMR spectrum obtained at elevated temperature is shown for the 10% sulfur system cured for 60 minutes at 150 ^{o}C. The result of fitting the NMR spectrum of Figure 5-12(a) with Lorentzian line shapes is shown in Figure 5-12(b). The difference between the two spectra obtained by a digital subtraction of the actual spectrum and the Lorentzian, is shown in Figure 5-12(c).

Peak areas were compared for the different curing times of the 10% sulfur-vulcanized system. The data was obtained by determining the area that each resonance peak contributes to the total area in each NMR spectrum. The data are tabulated in Table 5-6. With increasing cure time the peaks which appear at 57.5 and 44.6 ppm increase in intensity, while the resonance peak which appeared at 50.2 ppm no longer exists after 30 minutes of cure. The resonances which appear at 40.1, 16.1 and 14.0 ppm increase at generally the same rate with increasing cure time. The remaining new resonances show greater increases with further cure time.

The peak area data were also compared for the spectra of the 10%, 20% and 30% sulfur vulcanizates after 60 minutes of cure. The area contributions for all the resonance peaks observed in the spectra of these samples are tabulated in Table 5-6. The area of the peaks observed at 58 and 45 ppm increases significantly with increasing sulfur content. The resonances which appear at 38.6, 36.1, 30.0, and 18.0 ppm also increase. The remaining three resonances of interest which appear at 40.1, 16.1, and 14.0 ppm increase when the sulfur content is increased from 10% to 20%. Between 20% and 30%, the peak areas of these resonances remain relatively constant.

5.2.6. Relaxation Effects Due To Vulcanization. The spin-lattice (T^1) relaxation behavior of the sulfur-cured system was also studied. The T^1 behavior of 1,4-polyisoprene has been characterized in the past. Schaefer found that the spin-lattice relaxation times were: 50 (msec) for the methylene carbons, 95 (msec) for the methine carbons, 350 (msec) for the methyl carbons and 700 (msec) for the quaternary carbons (37). These values were obtained at 40 ^{o}C and 22.6 MHz. He also determined that there was little difference between the spin-lattice

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Table 5-6. Lorentzian Peak Areas (PPM)

	57.5	50.2	44.6	40.1	38.6	36.1	30.0	18.0	16.1	14.0
	D,S	A	C,S	T	S	S	T,S	M	T	M
10% Sulfur;										
5 min	.002	.001	.003						.001	.001
10	.008	.003	.007					.002	.001	.002
15	.016	.003	.015	.001				.006	.002	.002
30	.043	.003	.038	.005	.008	.007	.010	.008	.007	.006
60	.054		.056	.007	.013	.014	.020	.018	.012	.007
90	.074		.080	.012	.018	.016	.028	.020	.013	.010
20% Sulfur;										
30 min	.100		.096	.014	.019	.020	.030	.026	.016	.015
60	.130		.110	.015	.022	.024	.033	.028	.018	.018
30% Sulfur;										
30 min	.134		.129	.017	.035	.030	.040	.037	.020	.019
60	.178		.165	.018	.038	.033	.056	.042	.021	.020

D = Structure D from Table IV
A = Structure A from Table IV
C = Structure C from Table IV
S = Cyclic sulfide structure
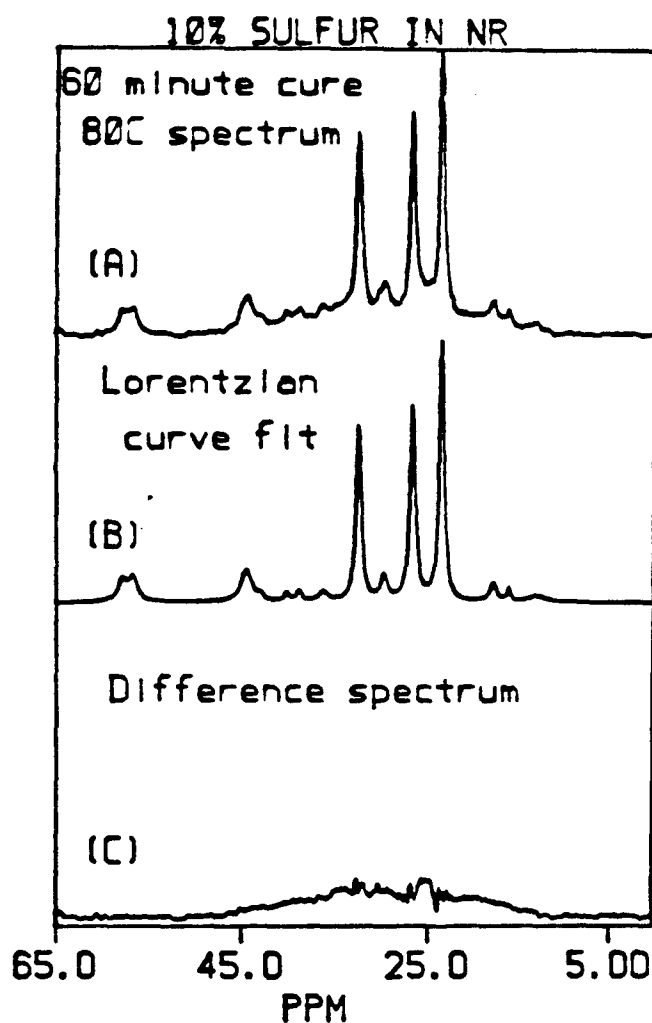T = Cis-to-trans isomerization
M = Methyl groups

Figure 12. (A) the C-13 GHPD/MAS NMR spectrum of natural rubber
cured with 10% sulfur for 60 mins at 150°C with the
measurement temperature at 80°C, (B) results of curve-
fitting the spectrum shown in (A) with Lorentzian
line shapes, (C) difference between spectrum shown in
(A) and spectrum in (B)

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relaxation times of polyisoprene when the system was crosslinked and carbon-black-filled, as compared to an unaltered system. However, it was observed that the linewidths were affected by the crosslinking and addition of carbon black to the system. Komoroski studied the T_1 relaxation behavior of butyl rubber which had been crosslinked to different extents (38). He found essentially no difference in the T_1 values of the carbons for the cured system as compared to the carbons in the uncured system. He also found no change in the C-13 NMR linewidths for the particular samples that were studied. In this study, linewidth changes have been observed with curing of the vulcanizates as has been previously noted. T_1s were measured for these systems by the standard inversion recovery method (180-t-90 pulse sequence) (39). The natural rubber carbons of the vulcanized systems have generally the same T_1 values as the carbons in the uncured natural rubber. T_1s were determined for the resonances which appear at 58 ppm and 45 ppm in the 10% sulfur vulcanized system. The peak which appears at 58 ppm has a T_1 time which is on the order of 800 msec. The peak observed at 45 ppm which is heavily overlapped when the sample is at room temperature has a T_1 of approximately 90 (msec).

5.3. Discussion

Our interest here is an attempt to unlock from the NMR spectra the chemical structure of the sulfur-vulcanized network. Consequently, we are interested in the kind and number of crosslinks as well as their distribution. The modifications to the natural rubber main chain induced by vulcanization such as cis-to-trans chain isomerization and conjugated unsaturation, are also of interest as it is clear that the ultimate properties of the rubber are influenced by the configuration and conformation of the main chain. Intra-chain or cyclic sulfide structures are also possibly induced by the vulcanization process. The NMR spectra can be obtained on the actual samples (filled or unfilled) so the information need not be extrapolated from the results of sulfur reactions on model olefins.

The NMR spectra are rich in spectral features and the primary burden is proper interpretation of the results in terms of structural modifications of the natural rubber by the sulfur chemistry.

5.3.1. Crosslinked Structure in Sulfur Vulcanized Natural Rubber.
When natural rubber is cured with sulfur alone, polysulfidic crosslinks are expected to occur as the predominant structural feature. Our C-13 NMR model compound studies indicate that disulfidic and trisulfidic crosslinks are indistinguishable from each other based on the current resolution of solid state NMR. As a result, a polysulfidic crosslink from the NMR perspective will

correspond to a group containing two or more sulfur atoms. Examination of the calculated chemical shifts found in Table 5-4 indicate that the resonances due to crosslinked carbons should appear in the aliphatic carbon region of the NMR spectra. The calculated range for monosulfidic crosslinks for the different carbon sites spans from 41 to 56 ppm. The carbon resonances for disulfidic/polysulfidic crosslinks, may be found in the range between 48 to 63 ppm. Based on these simple calculations, resonance peaks due to monosulfidic crosslinks may overlap with peaks due to polysulfidic crosslinks. Vicinal polysulfidic crosslinks will be detected only if the two individual links are found on adjacent carbons. Chemical shift calculations show that these types of crosslinks should appear roughly in the range between 56 to 70 ppm.

Elevating the NMR measurement temperatures of the vulcanized natural rubber samples increases the mobility and the resolution and thus permits a closer look at these systems. New resonances are distinguishable under these circumstances and can be assigned. Before crosslinking and at low levels of crosslinking, all resonances are clearly distinguishable, within 0.5 ppm. The vulcanization process generates new structures which produce additional resonance peaks and also loss of molecular motion in natural rubber. The result is broad unresolvable spectra. The higher measurement temperature studies have provided the same order of resolution in the NMR spectra as before the crosslinking process. The chemical shift frequencies for all the new resonances observed in the spectra are found in Table 5-6. The area contributions of the individual peaks to the total spectral area as determined by Lorentzian curve fitting, are included in this table. The areas represent the amount that each structure, if each peak is pure in the sense that it is generated by only one new species, is contributing to the sample. The data is only semi-quantitative because the NMR spectra do not necessarily reflect the entire vulcanizate sample for the highly cured systems. Therefore, the data is given as rough estimates of the detected structures. The error in the actual area measurements for the 10% sulfur samples which are cured less than 30 minutes is less than 10%. For the remainder of the samples, the error in the area measurement is estimated at 20%.

The resonances in the spectra of the 10% sulfur system are resolved up to a cure of 30 minutes. When this 30-minute cured sample was subjected to a measurement temperature increase, the resonance at 58 ppm split into two peaks and additional peaks in the aliphatic region of the spectrum were also resolved. The spectra of the samples after 60 and 90 minutes of cure are similar to the spectrum of the 30-minute cured sample except that the peak which appeared at 50 ppm is no longer observed. The peak at 50 ppm is assigned to the carbons involved in the polysulfidic

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crosslinks of structure A (the alkenyl carbon) in Table 5-4. Stucture A corresponds to an A^1-type structure. The sample cured with 10% sulfur for 30 minutes contains less than half a percent of this particular structure. Model compound studies have shown that this type of polysulfidic crosslink is commonly formed in sulfur vulcanizates. With the 20% sulfur system cured for 60 minutes, the same new peaks as in the 10% sulfur-vulcanized system appeared with an additional shoulder at 55 ppm. In the spectrum of the 30% sulfur system two new resonance peaks were observed at 33.4 and 25.2 ppm. These two peaks may be due to carbons adjacent to the carbons of the various crosslink points.

The resonance peak which appears at roughly 45 ppm in all the C-13 NMR spectra can be assigned to the polysulfidic crosslinks of structure C (the methyl carbon crosslink) in Table 5-4. The carbon-sulfur groups of the monosulfidic crosslinks of structure A may also overlap with this resonance peak. Due to the high levels of sulfur used in these samples, monosulfidic crosslinks probably do not occur to a large extent. The monosulfidic crosslinks of structure C would be expected to appear at roughly 42 ppm. Structure C is known as the B^1-type structure in the model compound studies. This crosslink type was the predominant structural feature found in model compound studies. For the 10% sulfur-cured samples, the area contribution of this resonance peak appearing at 45 ppm is 8% for the spectrum of the 90-minute cured sample. One crosslink may require two carbon-sulfur bonds of this type, which suggests that there is a 4% level of crosslinks with this particular structure in this sample.

The resonance peak which appears at 58 ppm in the C-13 NMR spectra arises from the crosslink point found in Structure D (the methylene carbon crosslink), which also corresponds to a B^1-type structure. In the high-measurement-temperature NMR spectra, this resonance was split into two peaks appearing at 57.5 and 56.5 ppm. Both resonances may be due to the same sulfidic structural feature found in different carbon configurations or conformations. Structure B where sulfur adds to the double bond of natural rubber, may also contribute to the resonance peak observed at 58 ppm. The chemical shift calculations show that a polysulfidic crosslink of this type will appear in this same spectral region. For the 10% sulfur vulcanizates, the structures which give rise to this peak are found at less than a 0.5% level after a 5-minute cure and a 7.5% level at 90 minutes of cure. Monosulfidic crosslinks bound as in structure D of Table 5-4 should be observed at approximately 50 ppm according to the chemical shift calculations. The levels of monosulfidic crosslinks in these vulcanizates appear to be too low for NMR detection. The crosslink structures which have been observed in this NMR study are shown in Figure 5-13. Vicinal crosslinks where polysulfidic crosslinks are found

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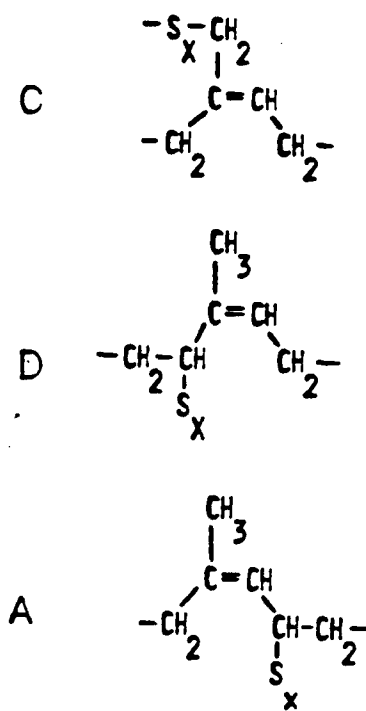
CHEMICAL SHIFTS (PPM)

	CALCULATED	OBSERVED
POLYSULFIDE (STRUCTURE C)	48.8	44.6
(STRUCTURE D)	57.7	57.5, 56.5
(STRUCTURE A)	51.9	50.2

Figure 13. Crosslink structures detected

on adjacent carbons have not been observed. For this particular structural feature one would expect two resonances between the spectral range of 56 to 70 ppm to occur. Vicinal crosslinks probably do not occur to an extent sufficient for spectroscopic detection at the current levels of NMR sensitivity.

The swell ratio data and the intensity data plotted in Figure 5-7 for the resonance peak which appears at 58 ppm, complement one another. The increase in swell ratio for samples cured longer than 30 minutes indicates a reduction in the density of crosslinks. The decrease in NMR intensity for the peak at 58 ppm also denotes a decrease in crosslinks, specifically polysulfidic crosslinks. This phenomenon corresponds to a process which commonly occurs in sulfur-vulcanized rubber and is known as reversion. Reversion is associated with the loss of physical and mechanical properties in vulcanized systems (40). During this process an inefficiently cured vulcanizate such as one crosslinked by sulfur only, undergoes desulfurization with extended cure or higher temperatures of curing (3). Fourier transform infrared spectroscopy has been used to determine the structural basis of the reversion process (41). The study concluded that the reversion process is associated with the formation of a trans-methine structure from the main chain arising from the desulfuration of the vulcanizate. As polysulfidic crosslinks are lost, the vulcanizate will be susceptible to further main chain modification. Cyclic sulfides may form at this point in the reaction.

The CP spectra of Figures 5-8(a) and 5-8(b) show additional resonances at roughly 81, 73 and 64 ppm. The resonance which is observed at 58 ppm in both the CP and the GHPD spectra is assigned to polysulfidic crosslinks. These crosslinks are expected to arise from structure D of Table 5-4. The three remaining resonances which are found in the CP spectrum of the 10% sulfur cured samples have not been observed in any of the other CP spectra. The 10% sulfur samples contained only sulfur while the 20% and 30% sulfur samples also contained 5 parts zinc oxide, 1 part antioxidant and 2.5 parts stearic acid. These additional resonances in the 10% sulfur-cured samples may be due to oxidation products resulting from the vulcanization process (42). Studies on polyisoprene oxidation have determined that epoxide, peroxide, hydroperoxide and alcohol structures may result in the structure (43). These structural features were observed between 60 to 90 ppm in the C-13 NMR spectra.

These assignments are consistent with previous literature. Komoroski et al. have done some NMR studies on sulfur-vulcanized natural rubber. They also observed new resonances at roughly 59 and 46 ppm for a sulfur-cured system, and used the (DEPT) pulse sequence in order to

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obtain additional information. DEPT is a spectral-editing
pulse sequence which allows one to distinguish resonances
which are due to methine, methylene and methyl carbons by
means of spin manipulation (44,45). The -CH- (methine)
subspectrum of Komoroski's sulfur vulcanized natural rubber
included the peak which appears at 59 ppm while the -CH$_2$-
(methylene) subspectrum included the resonance peak
observed at 46 ppm. The NMR signals in the DEPT spectra
were, however, considerably less intense than those in the
original (FID) spectrum. These results indicate that the
peak at 58 ppm arises for the most part from methine
carbons of the A^1-type polysulfide (structure D in Table
5-4) in the vulcanizate system. The peak at 45 ppm appears
to be due to methylene carbons in the B^1-type polysulfide
group (structure C).

5.3.2. Main Chain Structural Modifications in Sulfur
Vulcanized Natural Rubber. The unaccelerated sulfur
vulcanization of natural rubber is known to induce
structural main chain modifications. Cyclic sulfides
primarily occur as secondary products of the sulfuration
reaction. Both cyclic sulfides and conjugated hydrocarbons
are formed with the decomposition of polysulfides.
Chemical probe treatment of the sulfurated natural rubber
vulcanizates confirmed that a large percentage of sulfur
combined in the network was found in cyclic structures
(46,47). The actual structures of the cyclic sulfides have
been determined by model compound studies. The structure
of the most commonly formed cyclic sulfide is shown as
structure I of Figure 5-4. The calculated chemical shifts
for this structural feature are labeled. The new peaks
found at 38.6, 36.1, and 30.0 ppm and the shoulder
appearing at 43.0 ppm in the spectra are most probably due
to cyclic sulfides. These peaks appear after 30 minutes of
cure in the spectra of the 10% sulfur samples and are
observed for the 20% and 30% sulfur-vulcanized systems.
With reference to structure I in Figure 5-4, the four peaks
mentioned above may be due to methylene carbons found in
the cyclic sulfide. The new methyl group which arises
probably overlaps with one of the natural rubber carbon
resonances. According to the chemical shift calculations
the resonances for the different carbon groups of the
cyclic sulfides will also appear at higher fields. Thus,
the peaks at 58 and 45 ppm may have contributions from the
cyclic compounds in addition to the polysulfidic
crosslinks. Our data does not necessarily rule out any of
the cyclic structures shown in Figure 5-4. Based on the
area contributions of the peaks which arise at 38.6 ppm and
36.1 ppm, cyclic sulfides contribute roughly 2% to the
vulcanizate structure in the 10% sulfur sample cured for 90
minutes.

Cis-to-trans chain isomerization has been observed in all
of the vulcanizates of this study. The resonances which
appear at 40.1 and at 16.1 ppm correspond to the resonances

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found in the spectrum of the trans form of
1,4-polyisoprene. The peaks are assigned to the
g-methylene and the methyl groups, respectively of
trans-1,4-polyisoprene. The peak which appears at
approximately 30 ppm is assigned to the methylene unit
which is the connecting point between a cis and a trans
repeat unit of natural rubber. C-13 NMR studies on
cis-trans isomerized 1,4-polyisoprenes have shown that the
methylene carbon group between cis and trans repeat units
appear at roughly 31 ppm (48,49). These three resonances
are evidence of cis-to-trans isomerization which has been
observed in the past for these vulcanizates. According to
the area contributions of the peaks which appear at 40.1
and 16.1 ppm, 1% of the trans isomer of polyisoprene is
observed in the sample cured with 10% sulfur for 90
minutes. The resonance which appears at 30 ppm in the NMR
spectra probably has a contribution from cyclic sulfides as
was mentioned previously.

In this study, spectroscopic evidence for unsaturated
hydrocarbon has not been observed although clear FT-IR
evidence exists. New resonances in the olefinic region
(130-145 ppm) of the C-13 NMR spectra would be observed if
this structural feature occurred to a sufficient degree to
be detected by NMR in these vulcanizates. The new
resonances which appear at 18.0 and 14.0 ppm are assigned
to chain-end methyl groups. Additional methyl groups may
arise during the crosslinking process in these
vulcanizates. Methyl groups can be found at chain ends
arising from chain scission or bonded to the carbon groups
involved in the crosslinking.

In the peroxide-cured natural rubber vulcanizates,
Patterson et al., detected carbon-carbon crosslinks at
roughly 45 ppm in the C-13 NMR spectra. Past studies on
sulfur-cured natural rubber have shown that the crosslinks
are almost exclusively sulfidic. In these studies the
resonance which is observed at 45 ppm in the C-13 NMR
spectra has been assigned to carbon-sulfur bonds. But
carbon-carbon bonds cannot necessarily be ruled out.

5.3.3. Molecular Motion in Sulfur Vulcanized Natural
Rubber. Although we have used modern coherent averaging
techniques such as MAS and dipolar proton decoupling,
narrow lines are obtained with natural rubber using the
same NMR techniques as for liquids or solutions using
scalar decoupling. These narrow lines occur through
stochastic spatial averaging if there are molecular motions
with correlation times on the scale of $t < 10^{-8}$ seconds.
If the motion is anisotropic and any correlation time
exceeds 10^{-5} seconds the dipolar interaction broadens the
lines. As we will see, apparently motion in both ranges
are occurring in the vulcanized rubber system.

Many studies of polymers including dielectric and

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mechanical loss methods have been interpreted in terms of
molecular motions involving time scales which differ by
many orders of magnitude. Schaefer was the first to
interpret the NMR results in terms of a broad distribution
of motion in elastomers. He used a broad asymetric
distribution of correlation times to explain the NMR
relaxation times for polybutadiene and for polyisoprene.

For cis-1,4-polybutadiene, English and Dybowski suggest the
presence of a rapid, nearly isotropic, reorientation
associated with segmental motions of unentangled chain
segments and quite a slow motion associated with the
cooperative motion of the network segments (50). If this
motional model applies to the vulcanized natural rubber
system, as the number of chemical crosslinks increase, the
NMR linewidth should increase as we have observed.

The NMR spectra of the natural rubber crosslinked systems
exhibit an increase in linewidth with crosslinking as shown
in the spectra of Figure 5-6 and tabulated in Table 5-5.
The increase in linewidth with crosslinking has two
possibly different sources: 1) homogeneous broadening due
to a decrease in molecular motion of the crosslinked
network which contributes to broadening because the
chemical shift anisotropy and dipolar interactions are less
completely averaged, and 2) heterogeneous line broadening
by an increase in the number of isotropic chemical shift
contributions due to the large number of constrained
molecular configurations and conformations of the chain due
to the crosslinking. Previous work would suggest that the
increase in the number of chemically induced entanglements
would increase the contribution of the slow motion
component, broadening the lines. This motional
interpretation is further supported by the observation that
the homogenous line broadening can be partially removed by
raising the NMR measurement temperature or using a swelling
agent. The heterogenous residual component is less easily
removed although it is apparent that the measurement
temperature and swelling agent increase the cooperative
motion of the chain segments, thus decreasing the number of
restricted segments contributing to the isotropic chemical
shift.

Further evidence for the existence of residual static
components resulting from the slow, perhaps anisotropic
motions, is the ease of observation of the proton-enhanced
cross polarization spectra for the crosslinked systems.
The cross polarization experiment requires the presence of
a static dipolar component for polarization transfer.

Half-widths of the resonance peaks corresponding to the
natural rubber carbons were obtained for the series of
spectra shown in Figure 5-6. The half-widths were measured
by fitting Lorentzian line shapes to the actual NMR
spectra. The data is tabulated in Table 5-5. For the

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peaks which appear at 134.8, 125.3 and 23.6 ppm and are assigned to the quaternary carbons, methine carbons and methyl carbons, respectively, the largest half-widths coincide with the longest curing times. The methylene carbons with resonances appearing at 32.5 and 26.7 ppm, deviate from the above trend. These two resonances were heavily overlapped in the actual NMR spectra which introduces error into the Lorentzian curve fitting.

In Figure 5-8, the CP spectra should reflect the fairly rigid carbons in the system that experience the strong dipolar coupling. Static dipolar interactions are necessary for efficient cross polarization. For systems with significant chain mobility such as natural rubber, the necessary interactions are considerably reduced. For efficient cross polarization in such a system, the Hartmann-Hahn match for the carbon and proton frequencies must be maintained very accurately. This requirement was essential in order to obtain the CP spectra for the 10% sulfur vulcanizates cured for short times. The CP spectra have reduced signal-to-noise values as compared to the GHPD spectra.

For the case of the natural rubber samples cured with 30% sulfur, the CP spectrum of Figure 5-9 is very similar to the GHPD NMR spectrum. This spectral observation is found to contrast the C-13 NMR spectra obtained for the peroxide-cured vulcanizates. Patterson et al. obtained different spectra with the CP and the GHPD experiments. For the peroxide-cured systems, the CP spectra clearly emphasized that the crosslink sites were much less mobile than the remainder of the vulcanizate. The 30% sulfur-cured sample is inherently more rigid, i.e., the natural rubber appears to have formed a more complex network with more extensive structural modifications than the natural rubber cured with 10% sulfur. The lack of spectral resolution in the GHPD spectra of Figure 5-9 is due to the increase in chemical shift dispersion and also to the lack of molecular motion in the system. The spectral overlap in the CP spectrum is due to resonances which arose during the curing process. The GHPD spectra reflect the regions of the sample that have molecular mobility, while the CP spectra tend to reflect the rigid regions. In the 30% sulfur-cured system the rigid regions appear to include a large number of the network species. Both the CP and GHPD NMR experiments readily yielded spectra for this highly cured system. These results may reflect the motional heterogeneity of crosslinked systems. Ford et al. studied crosslinked polystyrene gels using conventional C-13 NMR solution techniques (51). They observed that the signal area of the aliphatic resonances decreased with an increase in crosslinking. This was attributed to the structural heterogeneity of the carbon atoms contributing to any particular resonance. The heterogeneity in crosslinked polystyrene is due to

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sequencing differences and the various conformations
available to the system. In the sulfur-crosslinked
vulcanizates, certain sections of the sample may be more
rigid than other sections. The increased rigidity may be
due to a higher concentration of both monosulfidic and
polysulfidic crosslinks.

The formulations for the samples examined in this study are
listed in Table 5-7. The units are listed in parts per
hundred of natural rubber. The natural rubber used has the
technical classification SMR-5. Three different
accelerators were used for the different samples:
Tetramethylthiuram disulfide (TMTD),
N-oxydiethylene-2-benzothiazole sulfenamide (MOR) and
N-cyclohexyl-benzothiazole-2-sulfenamide (CBS). The
chemical structures of the accelerators that were utilized
in this study are shown in Figure 5-12. The accelerators
were obtained from the Monsanto Chemical Company. The
compounded natural rubber samples were prepared by mixing
the various components in a Brabender mixer head where the
temperature of the mixer head was maintained at 70 $^\circ$C for
30 minutes. The samples were then cured in a template with
a temperature-controlled hydraulic press at a pressure of
2,000 psi. The different temperatures and times of curing
are specified in the text. Equilibrium swelling

Table 5-7. Calculated Chemical Shifts (PPM)

Possible Structure	Mono	Di(Poly)
A	26.7+17.9=44.6	+25.2=51.9
B	33.1+17.9=51.0	+25.2=58.3
C	23.6+17.9=41.5	+25.2=48.8
D	32.5+17.9=50.4	+25.2=57.7
E	37.5+17.9=55.4	+25.2=62.7

measurements were carried out for all the samples in order
to determine the extent of crosslinking on a relative
basis.

5.4. General

Solid state C-13 NMR spectroscopy has been extended to the
study of the accelerated sulfur vulcanization of natural
rubber. Natural rubber vulcanizates which had been cured
with elemental sulfur only, were studied by this particular
technique. The NMR spectra that were obtained for these
systems provided significant structural information on the
natural rubber network. In this study, the samples are
formulated with sulfur, accelerators and activators in

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order to study the effects of the various components in the crosslinking process of natural rubber. The NMR spectra indicate that a simpler network structure is obtained with accelerated sulfur vulcanization as compared to the systems cured with high levels of elemental sulfur. Solution C-13 NMR model compound studies have indicated that polysulfides terminated by accelerator residues will be indistinguishable from polysulfidic crosslinks. In the natural rubber vulcanizates, polysulfidic crosslinks have been observed in addition to the pendant accelerator groups. Cis-to-trans chain isomerization has been found to occur in these vulcanizates.

Sulfur-vulcanized natural rubber systems have been studied by solid state C-13 NMR. This spectroscopic technique has provided for a structural characterization of the vulcanizates in their solid form. Samples have been analyzed for evidence of crosslink formation and main chain structural modification with the aid of appropriate pulse sequences in the C-13 NMR experiments. Polysulfidic crosslinks bound to the methyl and the methylene carbons of the natural rubber repeat unit have been observed. Other structural modifications which occur as a result of the vulcanization process were also detected. Five-membered cyclic sulfide structures are found in the natural rubber network, in addition to the observation of cis-to-trans chain isomerization. Moreover, the spectral broadening which is observed in the NMR spectra of the vulcanizates has been shown to have two origins. The overlapping line shapes are due to a decrease in molecular motion of the natural rubber chains and also to an increase in the chemical shift dispersion which arises from the new structural features that occur in the vulcanizate as a result of the curing process.

In this study the solid state C-13 NMR technique has been extended to study the accelerated sulfur vulcanization of natural rubber. The samples are prepared with a variety of formulations including accelerators and activators. The intent is to examine the effects of the various components in the compounding and curing of natural rubber. The solid state NMR results provide information on the final network structure of the accelerated vulcanizates. In the 1960s Campbell, Wise and Coran (52) developed characterization techniques to study the effects of compounding variables on accelerated sulfur natural rubber vulcanization. Some of their techniques allowed for an analysis of the reaction intermediates during the course of the vulcanization. Other methods were designed to provide data on the distributions of the types of crosslinks as well as on the number of crosslinks in the vulcanizates. Table 5-8 shows the formulations used.

To aid in the spectral assignments for the vulcanizates of this study, model compounds for accelerated

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sulfur-vulcanized natural rubber have been studied by solution C-13 NMR spectroscopy. The materials were obtained from Dr. M. Porter of the MRPRA. The model compounds are based on 2-methyl-2-pentene which has been selectively sulfurated. The systems that have been studied model the monosulfidic and disulfidic crosslinks and pendant accelerator groups. The model compounds are illustrated in Figure 5-14.

Chemical shift calculations were carried out in the previous NMR study for the sulfur-cured natural rubber systems. The calculated range for a monosulfidic crosslink was found to span from 41 to 56 ppm. For a disulfidic/polysulfidic crosslink the resonance peaks may be found in the spectral range between 48 to 63 ppm. Thus, it is possible that the expected ranges of the resonance peaks due to monosulfidic and polysulfidic crosslinks may overlap. A condensed compilation of the calculated chemical shifts from the previous work, is found in Table 5-7.

Table 5-8. Natural Rubber Formulations
            (units in parts per hundred)

Formulation	NR	S	ZnO	TMTD	CBS	MOR	AO	SA
10%TMTD in NR	100	--	--	10	--	--	--	--
10%TMTD;10%ZnO in NR	100	--	10	10	--	--	--	--
LS02-TMTD02	100	2	5	2	--	--	0.5	2.5
LS02-TMTD10	100	2	5	10	--	--	0.5	2.5
LS02-TMTD20	100	2	5	20	--	--	0.5	2.5
LS0.4-CBS6	100	0.4	5	--	6	--	0.5	1.0
LS2-CBS15	100	2	5	--	15	--	0.5	2.5
SS2-MOR	100	2	5	--	--	10	0.5	2.5
SS5-MOR	100	5	5	--	--	1	0.5	2.5

    NR   = Natural Rubber
    S   = Sulfur
    ZnO = Zinc oxide
    TMTD = Tetramethylthiuram disulfide
    CBS = N-cyclohexyl-benzothiazole-2-sulfenamide
    MOR = N-oxydiethylene-benzothiazole-2-sulfenamide
    AO   = Antioxidant
    SA   = Stearic acid

5.5. Results

5.5.1. Model Compounds. The chemical shifts of interest in the model compounds are those of the various carbon-sulfur linkages. The observed chemical shifts are tabulated in Table 5-7. The chemical shift calculations were obtained in the same manner as in the previous study. Sulfur shielding parameters were added to the initial
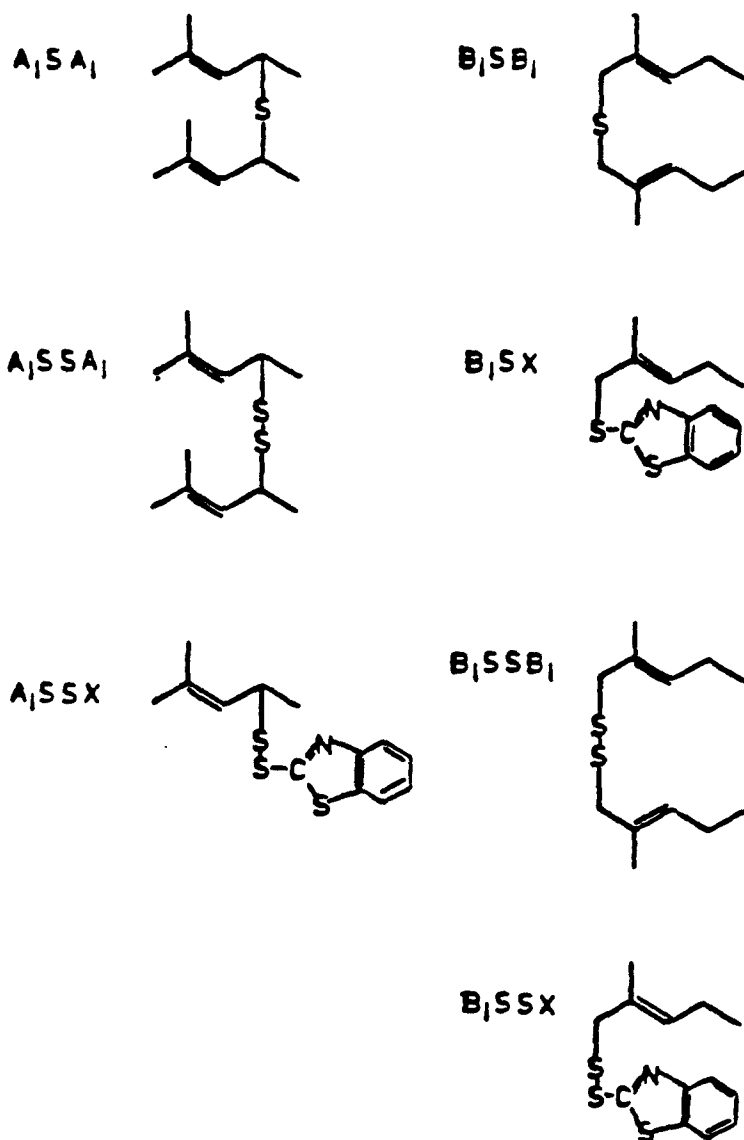
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MODEL SYSTEMS

$A_1 S A_1$

$B_1 S B_1$

$A_1 S S A_1$

$B_1 S X$

$A_1 S S X$

$B_1 S S B_1$

$B_1 S S X$

Figure 14. Compounds based on 2-methyl-2-pentene and studied as
models for sulfur-vulcanized natural rubber systems

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chemical shift values of the appropriate alkenes. The calculated chemical shifts for the model compounds are also found in Table 5-9.

Table 5-9. Observed and Calculated Chemical Shifts (PPM)

Model Compound	C-S bond	Observed Chemical Shift	Calculated Chemical Shift
A_1SA_1	HC-S-	36.8 ppm	21.5+17.9=39.4
A_1SSA_1	HC-S-S-	43.6;44.0 ppm	21.5+25.2=46.7
A_1SSX	HC-S-S-X	44.9 ppm	
B_1SB_1	H_2C-S-	40.0 ppm	25.7+17.9=43.6
B_1SSB_1	H_2C-S-S-	48.9 ppm	25.7+25.2=50.9
B_1SX	H_2C-S-X	42.9 ppm	
B_1SSX	H_2C-S-S-X	49.2 ppm	

X = accelerator residue

The observed chemical shift data obtained from the model compounds indicate several trends which may be extended to the C-13 NMR data of accelerated sulfur-vulcanized natural rubber. An interesting observation in the model compound NMR data is the effect that the pendant accelerator group has on the chemical shift of the carbon group to which it is bonded. In the A_1S-type system when the methine carbon is attached to the disulfide group as a part of a crosslink (A_1SA_1), the resonances corresponding to this carbon appear at 43.6 ppm and 44.0 ppm in the C-13 NMR spectrum. Two resonance peaks appear instead of one peak for this carbon type. This is attributed to the presence of both cis and trans isomers in the model compound. For the same system, when a pendant accelerator group, A_1SSX, is attached instead of the disulfidic crosslink, the resonance peak corresponding to the same methine carbon appears at 44.9 ppm. The difference between the two structures is approximately 1 ppm. For the B_1S-type systems, the chemical shift effect of the pendant accelerator group was studied for both the monosulfidic and the disulfidic groups. In this case a methylene carbon group is involved in the bonding. In the disulfidic case, B_1SSB_1, the resonance peak for the crosslinked methylene carbon appears at 48.9 ppm in the C-13 NMR spectrum while for B_1SSX, the peak for the same carbon appears at 49.2 ppm. The difference between the two chemical shift values for the disulfide is less than 1 ppm. Thus, it may not be possible to distinguish between a C-13 NMR resonance which is due to

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disulfidic crosslinks and a peak due to pendant accelerator groups which are connected to the natural rubber chain by two sulfur atoms. The resonance peaks for these two different structural features will most probably overlap in the NMR spectrum.

A larger chemical shift difference is observed for the monosulfidic bond. The methylene carbon of B_1SB_1 appears at 40.0 ppm while the same carbon group in B_1SX has a resonance which appears at 42.9 ppm. In this case the difference is approximately 3 ppm. The monosulfidic case of crosslink versus pendant group may be resolvable as indicated by the 3 ppm chemical shift difference. As the pendant accelerator group is further removed from the observed carbon, it will have less of an effect on the chemical shift. The monosulfidic linkage has a more pronounced effect as expected. Disulfidic/polysulfidic crosslink points will probably be relatively indistinguishable from disulfide/polysulfide pendant accelerator groups of any kind, while the monosulfidic counterparts may be resolvable.

In the previous study, the model compounds that were studied modeled the mono, di, and trisulfidic crosslinks of sulfur-vulcanized natural rubber. The spectroscopic results showed that for attachment to any particular carbon group, monosulfidic crosslinks should be distinquishable from disulfidic crosslinks by 7 ppm or more. The data indicate that disulfidic and trisulfidic crosslinks are probably not resolvable from each other. For purposes of NMR spectroscopy, a polysulfidic crosslink may contain two or more sulfur atoms. In summary, carbon-sulfur bonds which are a result of monosulfidic crosslinks should be readily distinquishable from carbon-sulfur bonds due to disulfidic/polysulfidic crosslinks. The same observation applies to the pendant accelerator groups.

5.5.2. Vulcanized Natural Rubber Systems. In order to compare the spectral effects of elemental sulfur-cured versus accelerated sulfur-vulcanized systems, natural rubber was crosslinked by equal amounts of sulfur in three different formulations.

In Figure 5-16, the C-13 GHPD/MAS NMR spectra of natural rubber vulcanized by the equivalent 0.01 moles sulfur per 100 grams natural rubber are shown. Spectrum A represents natural rubber cured with TMTD accelerator and zinc oxide (swell ratio = 3.5). Spectrum B is that of a sample cured with equal parts sulfur and TMTD accelerator and the other typical additives (swell ratio = 3.5). For the sample in the Spectrum C of Figure 5-16, only elemental sulfur was used as the curing agent (swell ratio = 8.3).

The vulcanizates were cured for 2 hours at 150 $^\circ$C. The spectra of Figure 5-16(b) and 5-16(c) closely resemble one

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another. The resonances at 57.5 ppm and at 44.6 ppm which appear in the NMR spectra of the samples where elemental sulfur was used in the curing formulation, do not appear in the spectrum of Figure 5-16(a). The TMTD;ZnO formulation is expected to generate a crosslinked structure consisting of monosulfidic and disulfidic crosslinks, with little main chain structural modification. In the previous studies on sulfur-vulcanized natural rubber systems, the resonance peaks at 57.5 and 44.6 ppm were assigned to polysulfidic crosslinks. The peak which appears at 57.5 ppm arises from structure D of Table 5-7, while the resonance at 44.6 ppm is due to structure C. The spectral results indicate a similar network for two of the vulcanizates (the samples corresponding to spectra B and C in Figure 5-16). Similar formulations as used for the samples of the spectra in Figure 5-16 are considered in the following paragraphs.

5.5.3. Sulfur Donor Accelerator System (no sulfur). TMTD is a sulfur donor and can be used to crosslink natural rubber without sulfur. The C-13 GHPD/MAS NMR spectrum of natural rubber cured with 10% TMTD and 10% zinc oxide is shown in Figure 5-17(a). This formulation is roughly equal to the one used for the sample corresponding to the spectrum in Figure 16A. Natural rubber was also cured with 10% TMTD by itself and the resulting NMR spectrum is shown in Figure 5-17(b). Both samples were cured at 150 ^{0}C for 90 minutes. Equilibrium swelling ratio measurements indicate that both samples are crosslinked and that the crosslink density in the natural rubber cured with 10% TMTD and 10% ZnO is significantly higher than for the system containing only TMTD. The swell ratio for the 10% TMTD system is 9.7, while for the TMTD;ZnO formulation the swell ratio value is 3.4. The smaller the ratio, the higher the degree of crosslinking for the vulcanizates. The five prominent resonances are due to the five different carbon groups of the natural rubber chain in both spectra. The natural rubber carbon resonances appear at 134.8, 125.3, 32.5, 26.7 and 23.6 ppm in the C-13 NMR spectra. For both systems the resonances due to the carbon groups of the natural rubber repeat unit are broadened when compared to the same resonances in the spectra of uncured natural rubber. The difference spectra, where contributions from the natural rubber peaks are digitally subtracted, are shown in Figure 5-18 for both of the vulcanizate systems shown in Figure 5-17. Three new resonances appear for the TMTD;ZnO curing system, at 40.1, 30.0 and 16.1 ppm in the spectrum of Figure 5-18(a). Five distinct new resonances for the TMTD cured sample appear in the C-13 NMR spectrum of Figure 5-18(b). The chemical shift positions of these resonances are: 57.5, 44.6, 40.1, 30.0, and 16.1 ppm.

Integrated peak areas were determined for the resonance peaks observed in the NMR spectra of the vulcanizate samples. The data was obtained by determining the integrated area for all the resonances observed in the NMR

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ACCELERATORS

TETRAMETHYLTHIURAM DISULFIDE (TMTD)
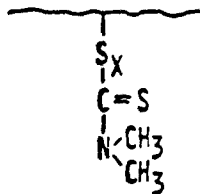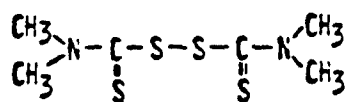
N-OXYDIETHYLENE-BENZOTHIAZOLE-2-SULFENAMIDE (MOR)
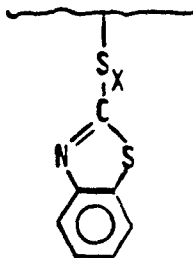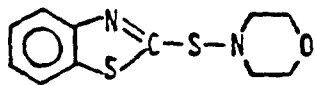
N-CYCLOHEXYL-BENZOTHIAZOLE-2-SULFENAMIDE (CBS)
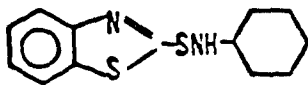
Figure 15. Chemical structures of the organic accelerators used in this study. Structures of accelerators as pendant groups
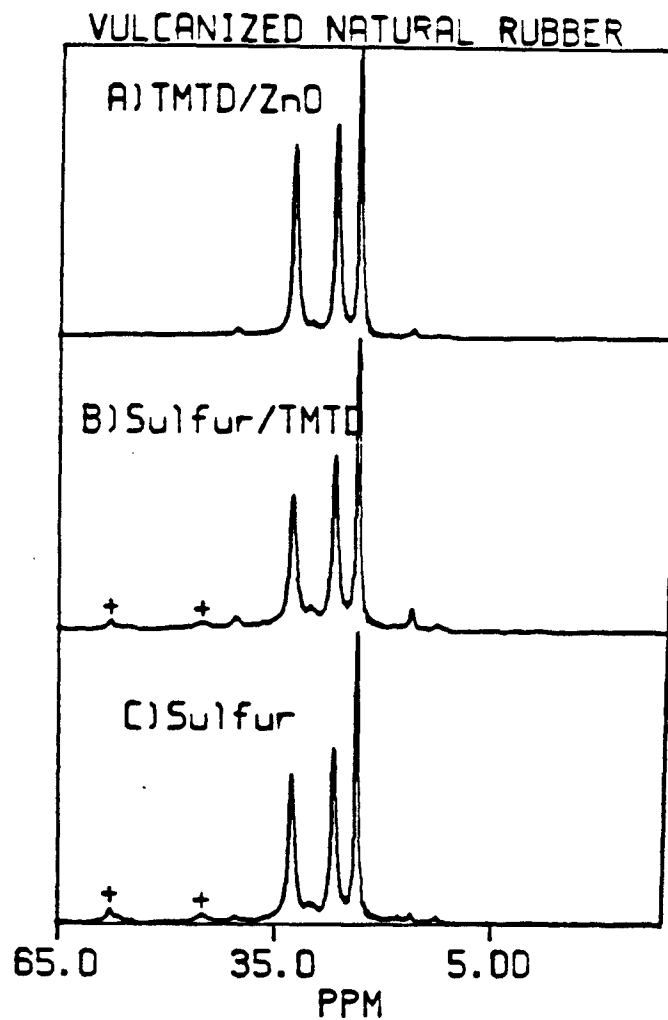
Figure 16. The C-13 GHPD/MAS NMR spectra of natural rubber vulcanized with 0.01 moles sulfur to one hundred parts natural rubber for 2 h at 150°C. (A) spectrum of sample cured with tetramethylthiuram disulfide (TMTD) accelerator and zinc oxide (swell ratio = 3.5). (B) spectrum of sample cured with equal amounts of sulfur and TMTD (swell ratio = 3.5). (C) spectrum of sample cured with elemental sulfur (swell ratio = 8.3).
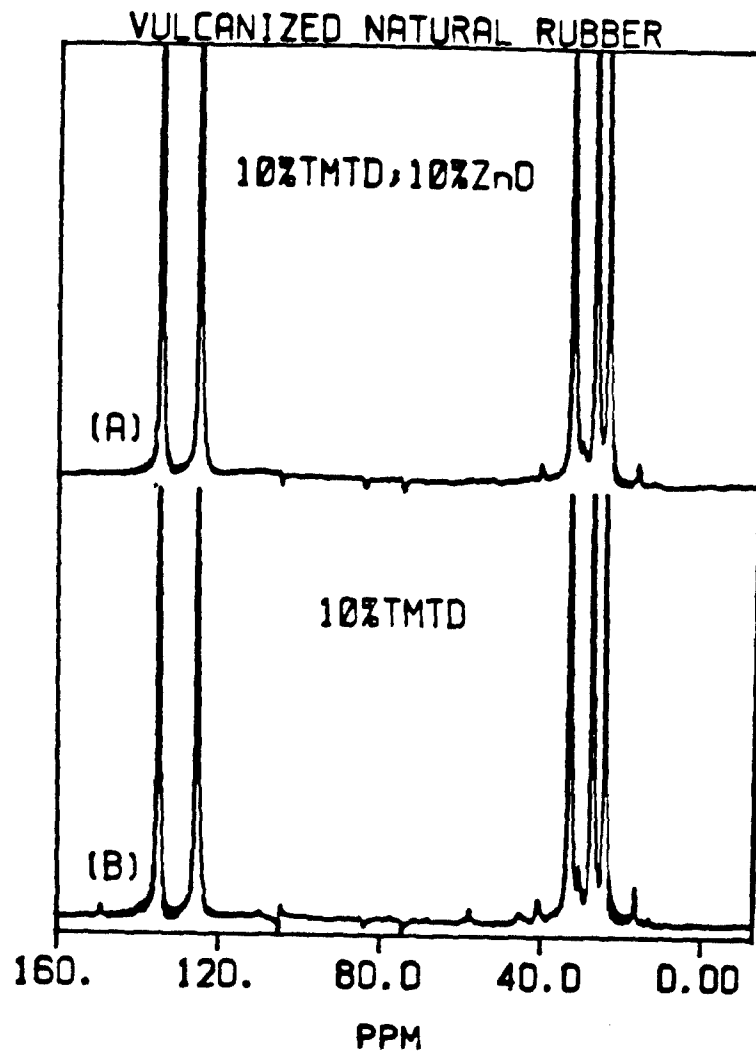
Figure 17. The C-13 GHPD/MAS NMR spectra of natural rubber vulcanized at 150°C for 90 mins. (A) spectrum of sample cured with 10% TMTD and 10% ZnO, and (B) spectrum of sample cured with 10% TMTD accelerator

spectra. The data found in Table 5-10 represents the area that each individual resonance peak contributes to the total spectral area in each NMR spectrum. The error in the data is estimated at roughly 10%. The integrated peak areas for the 10% TMTD;10% ZnO vulcanizates are roughly the same for all three new resonances at the different cure times. For the 10% TMTD system, small area increases are observed for the new peaks with increasing cure time. The spectral changes that arise with the TMTD-cured system are more pronounced than the changes in the NMR spectra of the TMTD;ZnO system.

Half-widths of the resonance peaks corresponding to the natural rubber carbons were obtained for all the NMR spectra of the vulcanizates. The half-widths were measured by fitting Lorentzian line shapes to the actual NMR spectra. This particular method was used in order to compare the data of this study to the previous study. Lorentzian shapes accurately approximate the NMR spectra. The data is tabulated in Table 5-11. The natural rubber carbon resonances in the spectra of the vulcanizates are broadened in comparison with the same resonances of the uncured natural rubber. The half-widths of the methine and the methylene carbons of natural rubber change most significantly between formulations and with increasing cure time.

5.5.4. Accelerator/Sulfur Systems. Varying ratios of sulfur to accelerator were used in the natural rubber formulations. TMTD was the primary accelerator utilized in these studies. The samples were cured for various lengths of time and then studied by C-13 MAS NMR. The spectrum obtained from a sample cured with equal amounts of sulfur and crosslinking accelerator (LS02-TMTD02) is shown in Figure 5-19(a). This formulation is approximately equal to the formulation used for the sample corresponding to the spectrum in Figure 5-16(b). The spectrum of Figure 5-19(b) is the result of digitally subtracting out the natural rubber peaks from the spectrum of Figure 5-19(a). New resonances for the sulfur/TMTD curing system are observed at 57.5, 44.6, 40.1, 30.0, 16.1 and 14.0 ppm.

The C-13 GHPD NMR spectrum of LS02-TMTD10, a formulation containing a high ratio of accelerator to sulfur, is shown in Figure 5-20(b). Six new resonances appear with the curing process and are observed at 57.5, 44.6, 40.1, 30.0, 16.1, and 14.0 ppm in the aliphatic region of the NMR spectrum. The new resonances observed for this particular sample are generally the same as for the LS02-TMTD02 system (Figure 5-19(a)) and the 10% TMTD system (Figure 5-17(b)). If this same sample is postcured at 180 $^\circ$C for one hour, the resulting NMR spectrum shows increased linewidths in the aliphatic carbon region as is shown in Figure 5-20(a). In this case three of the resonance peaks found at 40.1, 16.1 and 14.0 ppm which were initially observed in the

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Table 5-10. Peak Area Data

Samples	Temp	Time	Integrated Peak Area (ppm)				
			57.5 D	44.6 C	40.1 T	30.0 T	16.1 T
10% TMTD;	150°C;	30 min	.006	.005	.005	.003	.004
		60	.007	.006	.007	.004	.005
		90	.008	.007	.008	.006	.008
	140°C;	9 hrs	.010	.008	.009	.007	.010
10% TMTD+	150°C;	30 min			.003	.004	.003
10% ZnO		60			.004	.003	.004
		90			.004	.004	.005
	140°C;	9 hrs			.005	.004	.005
LS02-TMTD02;	150°C;	30 min	.003	.004	.004	.004	.004
		60	.004	.005	.004	.003	.004
		90	.005	.004	.006	.004	.004
		5 hrs	.005	.006	.005	.005	.006
LS02-TMTD10;	150°C;	30 min	.008	.005	.006	.006	.006
		60	.009	.005	.005	.006	.005
		90	.012	.008	.009	.008	.008
		5 hrs	.013	.007	.011	.007	.010
LS02-TMTD20;	150°C;	30 min	.009	.009	.008	.010	.012
		60	.010	.008	.010	.009	.011
		90	.012	.010	.010	.011	.013
	150°C;post;	90	.017	.012	.015	.013	.015

D = Structure D from Table I
C = Structure C from Table I
T = Cis-to-trans isomerization
M = Methyl groups

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Table 5-11. Half-Width of Natural Rubber Resonances Obtained
             by Lorentzian Curve-Fitting (PPM)

|	-C= 134.8ppm	=CH- 125.3ppm	-CH$_2$- 32.5ppm	-CH$_2$- 26.7ppm	-CH$_3$ 23.6ppm
NATURAL RUBBER	0.19	0.23	0.29	0.27	0.20
10% TMTD;					
150°C; 30 min	0.24	0.31	0.38	0.34	0.25
60	0.22	0.28	0.34	0.30	0.21
90	0.22	0.29	0.37	0.32	0.21
140°C; 9 hrs	0.24	0.32	0.40	0.34	0.22
10% TMTD;10%ZnO;					
150°C; 30 min	0.21	0.29	0.39	0.33	0.22
60	0.22	0.29	0.37	0.32	0.22
90	0.25	0.31	0.39	0.34	0.25
140°C; 9 hrs	0.23	0.31	0.39	0.34	0.23
LS02-TMTD02;					
150°C; 30 min	0.21	0.28	0.34	0.31	0.21
60	0.23	0.34	0.48	0.39	0.23
90	0.24	0.32	0.41	0.35	0.24
5 hrs	0.25	0.33	0.41	0.36	0.25
LS02-TMTD10;					
150°C; 30 min	0.24	0.32	0.42	0.36	0.25
60	0.24	0.35	0.44	0.38	0.23
90	0.25	0.39	0.47	0.39	0.22
5 hrs	0.27	0.45	0.65	0.55	0.28
LS02-TMTD20;					
150°C; 30 min	0.25	0.37	0.45	0.39	0.24
60	0.25	0.34	0.42	0.37	0.27
90	0.27	0.45	0.56	0.49	0.27
post; 90 min	0.44	0.69	0.62	0.57	0.38
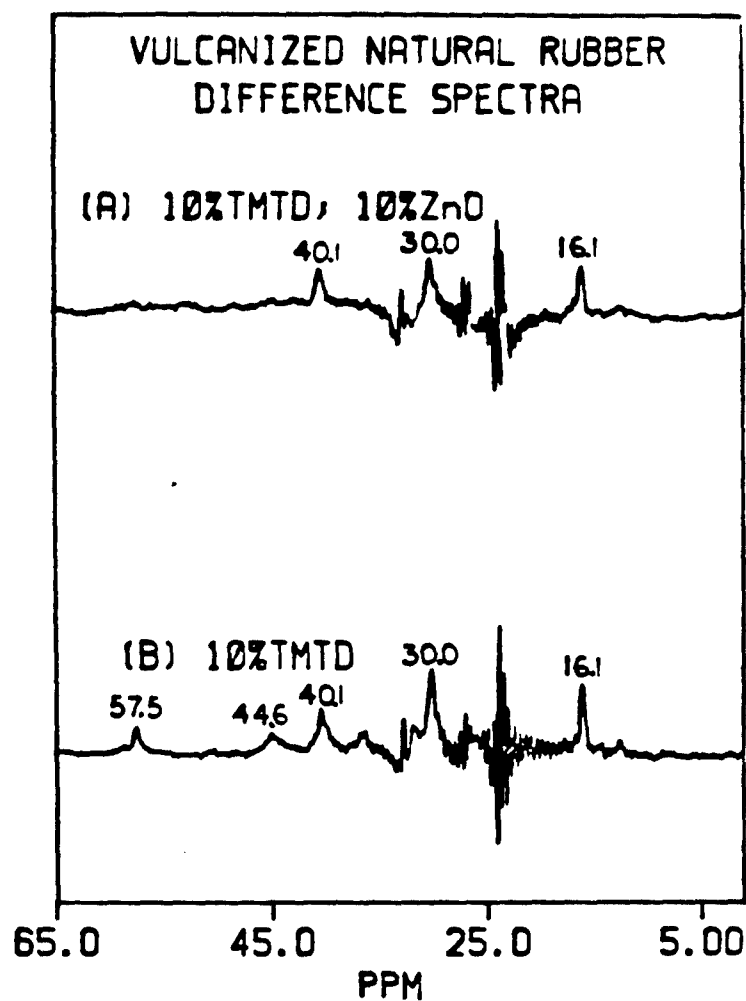
Figure 18. Difference spectra obtained from the spectra found in figure 4. Natural rubber peak contributions were digitally subtracted
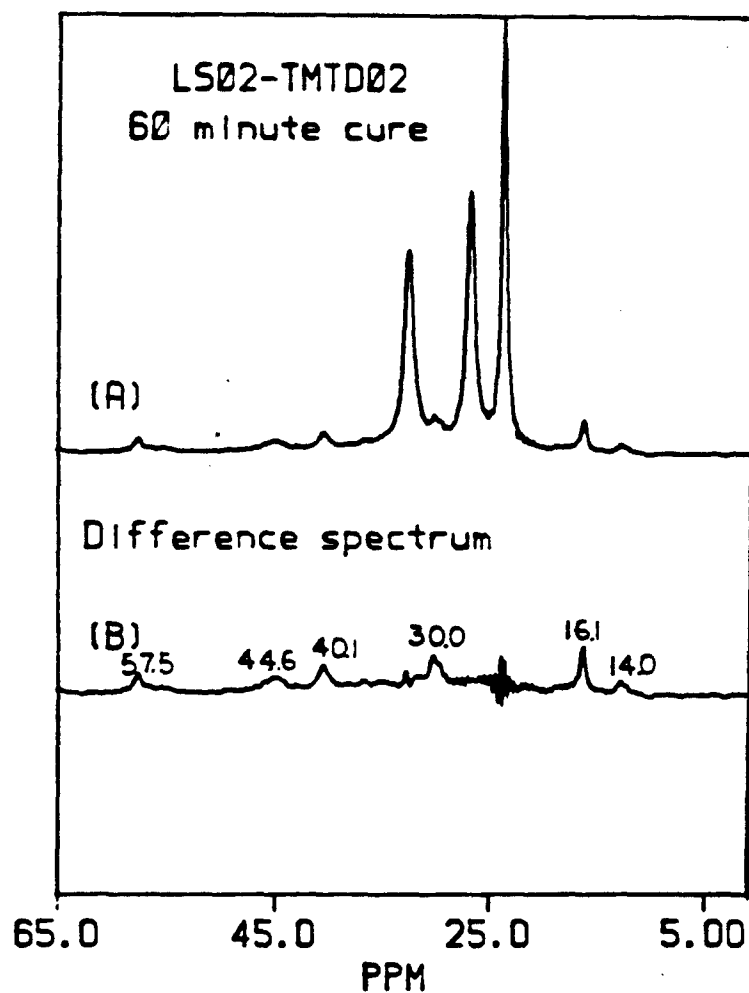
Figure 19. The C-13 MAS NMR spectra of natural rubber cured with 2 parts sulfur to 2 parts TMTD accelerator (LS02-TMTD02) at 150°C for 90 mins. (A) GHPD spectrum and (B) difference spectrum where natural rubber resonances were digitally subtracted.

spectrum of Figure 5-20(b), have increased in intensity.
An additional resonance appears at 36.4 ppm. The
difference spectrum obtained by a digital subtraction of
the spectrum of Figure 5-20(b) from the spectrum of Figure
5-20(a) is shown in Figure 5-20(c). If the same
vulcanizate formulation (LS02-TMTD10) is cured for 5 hours
at 150 $^\circ$C, the NMR spectrum obtained for this sample is
generally the same as the spectrum found in Figure 5-20(a).

Vulcanizates formulated with 20 parts TMTD to 2 parts
sulfur were also analyzed (LS02-TMTD20). The new
resonances which arise with curing in this system,
correspond to the same resonances observed for the
LS02-TMTD10 and LS02-TMTD02 systems. The peak area data
are tabulated in Table 5-10 for all the samples. This data
represents the area contributions of the individual peaks
to the total spectral area for each NMR spectrum. The data
show that increases in the level of TMTD accelerator used
in the different formulations result in increases in the
peak area for the resonances which appear at 57.5 and 44.6
ppm. The contributions of the peaks appearing at 40.1,
30.0 and 16.1 ppm also show corresponding increases.

The spin lattice (T_1) relaxation behavior has been studied
for several of the sulfur/TMTD accelerator vulcanization
systems. T_1s have been measured by the standard inversion
recovery method (180-τ-90 pulse sequence). The NMR spectra
obtained from this experiment for the LS02-TMTD10 system
cured at 150 $^\circ$C for 60 minutes are shown in Figure 5-21.
The natural rubber carbons of the vulcanized system have
generally the same T_1 values as the carbons of the uncured
natural rubber. This phenomenon was also observed for the
10% sulfur-cured natural rubber systems of the previous
work. Spin-lattice relaxation times have been determined
for the new resonances which appear at 57.5 ppm, 44.6 ppm,
40.1 ppm and 16.1 ppm. The peak which appears at 57.5 ppm
has a T_1 value of roughly 800 (msec) while the peak
observed at 45 ppm has a T_1 of 90 (msec). The resonances
which are observed at 40.1 ppm and at 16.1 ppm have
spin-lattice relaxation times which were determined to be
45 (msec) and 575 (msec), respectively. These relaxation
times correspond to the T_1 times determined for two of the
carbon groups of trans-1,4-polyisoprene. One of the
methylene groups of trans-1,4-polyisoprene appears at
roughly 40 ppm while the methyl groups are observed at 16
ppm in the C-13 NMR spectra. The same spin-lattice
relaxation behavior was observed for the 10% TMTD-cured
natural rubber (spectrum in Figure 5-17(b)) and for the
LS02-TMTD02 formulation (spectrum in Figure 5-19(a)).

Two additional accelerators were used for different
formulations in the study. A common accelerator used in
the processing of vulcanizates is CBS. This accelerator
was used in a formulation which is known to produce a high
percentage of monosulfidic crosslinks in natural rubber.
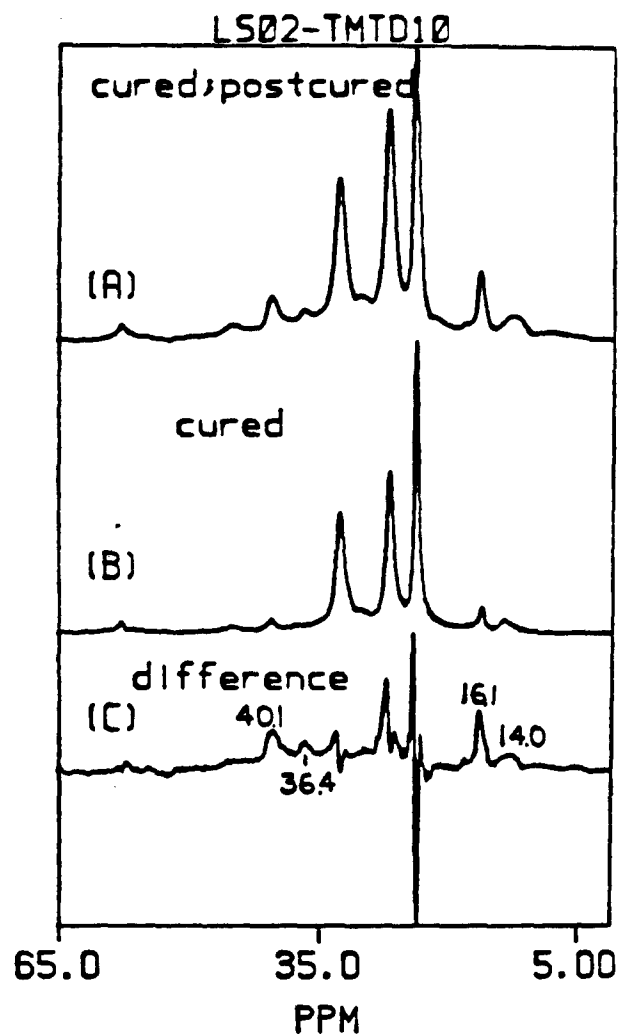
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Figure 20. The C-13 GHPD/MAS NMR spectra of natural rubber cured with 2 parts sulfur and 10 parts TMTD accelerator (LS02-TMTD10) (A) spectrum of sample cured for 90 mins at 150°C then postcured at 180°C for 60 mins, (B) spectrum of sample cured for 90 mins at 150°C, (C) difference spectrum (A)-(B).
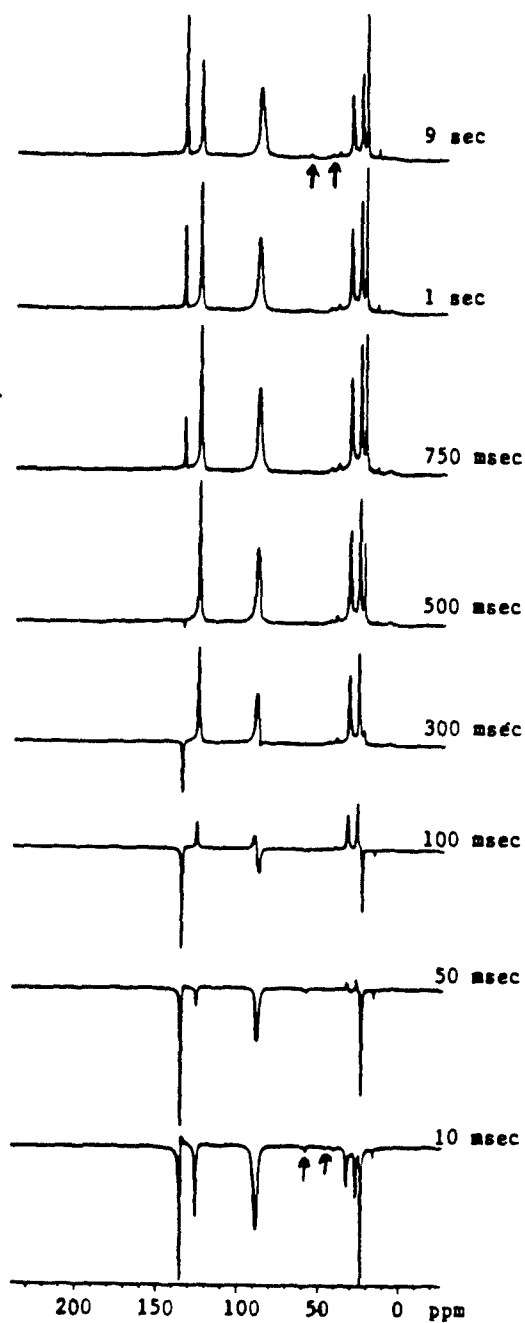
Figure 21. T_1 - Inversion recovery results for the LS02-TMTD10 sample

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The resulting C-13 GHPD/MAS NMR spectrum obtained for this particular formulation cured at 140 $^\circ$C for 2 hours is shown in Figure 5-22(a). Minimal spectral changes are observed when compared to the C-13 NMR spectrum of uncured natural rubber. The aliphatic carbon region of the NMR spectrum for this system shows new resonances appearing at 40.1 and 16.1 ppm. In a subsequent study the amounts of sulfur and accelerator used in the formulation were increased. The resulting C-13 GHPD/MAS NMR spectrum of LS2-CBS15 closely resemble the spectra obtained for LS02-TMTD02 and LS02-TMTD10 vulcanizate samples.

In Figure 5-22(b), the C-13 NMR results of a natural rubber sample cured with 5 parts sulfur to 1 part MOR curing accelerator are shown. MOR is another commonly used curing accelerator in the rubber industry. It was utilized in this study in order to determine the spectral effects of the accelerators. In this case seven additional resonance peaks are evident and appear at 57.5, 44.6, 40.1, 30.0, 18.0, 16.1 and 14.0 ppm. For the most part these new resonances correspond to the resonances found for the LS02-TMTD10 system. A natural rubber formulation was also cured with 5 parts MOR to 1 part sulfur. The resulting C-13 GHPD/MAS NMR spectrum resembles the spectrum obtained from the system cured with 10% TMTD;10% ZnO formulation (Figure 5-17(a)).

5.6. Discussion

5.6.1. Sulfur Vulcanization Versus Accelerated Sulfur Vulcanization of Natural Rubber. We were interested in determining the spectral effects of the accelerators in the sulfur vulcanization of natural rubber. The three NMR spectra shown in Figure 5-16 represent the general network structures of the systems studied. Spectrum B (sulfur/TMTD cure) and spectrum C (sulfur cure) are very similar but the crosslink densities as indicated by the swell ratios are different. Based on previous studies, polysulfidic crosslink points can be assigned to the resonances appearing at 57.5 and 44.6 ppm in both systems. In the TMTD;ZnO-cured vulcanizate (spectrum A in Figure 5-16), peaks that may be assigned to crosslink points are not observed. A high percentage of monosulfidic crosslinks is expected for this system. Past model compound data has shown that structures A (methine carbon crosslink), C (methylene carbon crosslink), and D (methine carbon crosslink) of Table 5-7, should predominate with the sulfur vulcanization of natural rubber. Thus, monosulfidic crosslinks are expected at roughly 45 ppm, 42 ppm and 50 ppm, respectively. Monosulfidic crosslinks have not necessarily been observed in any of the systems studied. There are several explanations for this. For the vulcanizates in which they are most likely to occur, the crosslink density is too low for current NMR sensitivity. In the NMR spectra of the vulcanizate systems where new
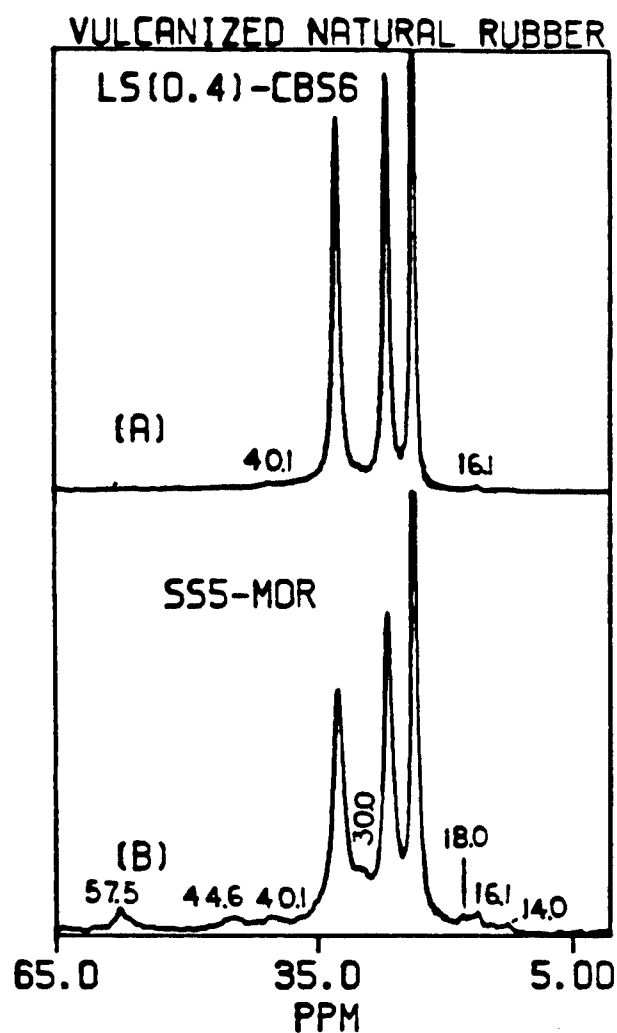
Figure 22.   (A) the C-13 GHPD/MAS NMR spectrum of natural rubber
cured with the CBS accelerator (LS.4-CBS6) at 140°C
for 2 h, (B) the C-13 GHPD/MAS NMR spectrum of natural
rubber cured with the MOR accelerator (SS5-MOR) at
150°C for 90 mins

resonances are observed, the levels of sulfur that are used in the formulations are higher that necessary to obtain a crosslinked system. In these cases polysulfidic crosslinks would predominate with possible overlap from monosulfidic crosslinks as has been noted before.

When accelerators are used in the vulcanization of natural rubber, crosslinking precursors precede the formation of crosslinks. The formation of an activating sulfurating agent by reaction of a sulfur donor (which can also be an accelerator as in the case of TMTD) and zinc oxide, or sulfur and an accelerator complex, is postulated to be the first step in vulcanization. The sulfurating agent reacts with the rubber to generate a rubberbound polysulfidic pendant group. As a result of this step of the reaction, sulfides are bound to the natural rubber chain and terminated by the accelerator residue. A considerable amount of effort has been directed toward studying pendant accelerator groups in rubber vulcanizates. The number of pendant groups observed in the resulting network structure increases with an increase in the amount of the accelerator used in the formulation. These rubber bound intermediates further react to form polysulfidic crosslinks which can subsequently undergo a series of network maturing reactions. A vulcanizate cured in an accelerated sulfur formulation will probably contain a combination of sulfide-terminated pendant groups and crosslinks of different sulfur rank. For more than one sulfur atom in a linkage, the C-13 NMR model compound studies have shown that polysulfidic crosslinks are indistinquishable from polysulfides terminated by accelerator residues. The resonances observed at 57.5 ppm and at 44.6 ppm in spectrum B of Figure 5-16 are assigned to both polysulfidic crosslink points and to pendant accelerator groups.

5.6.2. Sulfur-Donor Vulcanization of Natural Rubber. Our approach was to look at the simplest curing system and then to add to it. The TMTD;ZnO vulcanizates and the TMTD vulcanizates were examined before adding elemental sulfur to the accelerated curing formulations. In the initial stages of these C-13 NMR studies there was some concern that the resonances from TMTD itself would appear in the C-13 NMR spectra of the vulcanizates. In order to obtain the NMR spectrum of TMTD under the same spectral and pulse sequence conditions that have been used during the course of these studies, long scans are required. The resulting spectrum of TMTD shows resonances at approximately 42 ppm for the methyl groups of the compound. It is safe to say that peaks due to unreacted TMTD are not interfering with the resonances in the spectra.

Considerable spectral differences are observed for the spectra of the two different formulations utilizing the sulfur donor (TMTD) systems in Figures 5-17 and 5-5. Three new peaks appear for the 10% TMTD;10% ZnO formulation.

According to the data of Table 5-10 these resonances appear
with approximately equal spectral areas. The resonances
which appear at 40.1 and 16.1 ppm correspond to the
resonances found in the spectrum of the trans form of
1,4-polyisoprene and are assigned to the g-methylene and
the groups, respectively of trans-1,4-polyisoprene. The
peak appearing at approximately 30 ppm is assigned to the
methylene unit which is the connecting point between a cis
and a trans repeat unit of natural rubber. C-13 NMR
studies on cis-trans isomerized 1,4-polyisoprenes have
shown that the resonance of the methylene carbon group
which is found between the cis and trans repeat units will
appear at roughly 31 ppm. These three resonances are
evidence of cis-to-trans chain isomerization which has been
observed in the past for these vulcanizates.

Natural rubber crosslinked with 10% TMTD and 10% zinc oxide
is expected to produce a network structure containing
monosulfidic crosslinks and little main chain modification.
Resonance peaks due to crosslink points or crosslink
precursors have not been detected in this system. It is
probable that the crosslink density in these particular
vulcanizates is too low for the sensitivity of this NMR
experiment.

In the spectrum of Figure 5-17(b) two resonances appear in
addition to the same new resonances observed in the
spectrum of Figure 5-17(a). TMTD can react with
polyisoprene in the absence of zinc oxide. But past
results also show that crosslinking does not take place to
any appreciable extent with only the TMTD accelerator used
in the vulcanizate formulation. The swelling measurements
of this study also indicated that the 10% TMTD-cured
vulcanizate was very lightly crosslinked. Using the
chemical shift calculations and the results of the model
compound studies, the resonances which appear at 57.5 ppm
and 44.6 ppm can be assigned. Both resonance peaks appear
to arise from sulfides which are chemically bound to the
natural rubber chain and terminated by pendant accelerator
groups. The resonances observed in the spectrum of the
TMTD only system probably do not arise from crosslink
points. The peak which is observed at 57.5 ppm indicates
the attack of a polysulfide at the g-methylene carbon,
while the resonance observed at 44.6 ppm indicates a
reaction with the methyl carbon of natural rubber. These
two structures correspond to structures D and C shown in
Table 5-7. The peak area data indicate that there is
roughly 1% of these two structures present. The areas
represent the amount that each structure, if each peak is
pure in the sense that it is generated by one new species,
is contributing to the sample. The different extents or
temperatures of cure do not appear to have large effects on
the peak areas of this particular system. But small
relative peak area increases are observed for all the new
resonances.

The presently accepted scheme of vulcanization requires the formation of a zinc sulfurating agent. This active zinc sulfurating agent reacts with rubber to produce accelerator-terminated sulfides which lead to crosslink formation. However, the results of these C-13 NMR studies have shown that pendant groups can form without zinc oxide. The zinc oxide may not be required in the reaction leading to the formation of crosslink precursors but it certainly accelerated the reactions.

5.6.3. Accelerated Sulfur Vulcanization of Natural Rubber. The natural rubber systems crosslinked with accelerated formulations appear to show a simpler network structure than the vulcanizates cured with only high sulfur levels. This is indicated by a comparison of the C-13 GHPD/MAS NMR spectra of Figures 5-16(b), 5-17 through 5-20, to the spectra obtained from natural rubber cured with only high sulfur levels. Accelerated sulfur vulcanization where the levels of crosslinking accelerator to elemental sulfur are very high, result in network systems containing a large percentage of monosulfidic crosslinks. These types of accelerator-formulated systems should have few main chain modifications such as cyclic sulfide structures, cis-to-trans chain isomerization and conjugated unsaturation, than found in vulcanizates formulated with high sulfur levels. Thus, main chain structural modifications are not expected to occur to a large extent in the accelerated systems studied. Cis-to-trans chain isomerization has been detected as was mentioned. The resonances which appear at 40.1, 30.0 and 16.1 ppm represent this occurrence. Conjugated unsaturation has not been observed in any of these systems or the vulcanizates of the previous study. It appears that the extent of unsaturated hydrocarbon is too low for NMR detection. Cyclic sulfides are found in very small amounts with accelerated vulcanization. In these studies, evidence for the cyclic sulfide structure was observed upon the post curing of a vulcanizate sample.

The levels of sulfur and accelerator used in these formulations are higher than necessary for vulcanization (52). As a result the primary structural feature is found to be a polysulfide. The peaks which appear at 57.5 and 44.6 ppm are observed in the same spectral position as the resonances due to polysulfidic crosslinks of the previous study. The addition of accelerators in the vulcanization formulations indicates that polysulfides terminated by accelerator residues are likely main chain modifications. Thus, the resonances at 57.5 and 44.6 ppm are probably due to both types of sulfides.

As was mentioned previously and is obvious from Table 5-7, monosulfidic crosslinks may overlap with polysulfides. The high sulfur levels tend to indicate that monosulfidic crosslinks will not be observed in these systems.

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Patterson et al. detected carbon-carbon crosslinks at roughly 45 ppm in the solid state NMR spectra of peroxide-cured natural rubber vulcanizates. In these studies the resonance at 45 ppm has been assigned to carbon-sulfur bonds since carbon-carbon crosslinks are not likely structural features according to past studies. But, carbon-carbon bonds cannot necessarily be ruled out.

For systems containing equal and high ratios of accelerator to sulfur, the C-13 MAS/GHPD NMR spectrum as shown in Figures 5-19 and 5-20 are similar to the spectrum obtained for the natural rubber system cured with 10% TMTD in Figure 5-17(b). Cis-to-trans chain isomerization is evident with peaks at 40.1, 30.0 and 16.1 ppm. The peak which occurs at 14.0 ppm is assigned to additional methyl groups which may arise during the crosslinking process. Methyl groups can be found at chain ends because of chain scission or bonded to the carbon groups involved in crosslinks. The peaks at 57.5 ppm and at 44.6 ppm are due to carbon-sulfur bonds. These bonds may arise from the natural rubber carbons which are bound in polysulfidic crosslinks. They may also arise from polysulfides which are terminated by pendant accelerator groups. The particular structures that were observed in the sulfur-cured vulcanizates of the previous study, and which are observed for the systems of this study correspond to structures D and C of Table 5-7. According to the peak area data there is less than half a percent of each structure in the sample cured with equal parts sulfur and accelerator. Generally, an increase in the amount of TMTD accelerator used in the formulation resulted in an increase in the peak area of the new resonances observed in the NMR spectra.

The C-13 NMR spectrum of the postcured material in Figure 5-20(a) indicates the occurrence of further structural modifications. Spectral broadening is observed as a result of the loss of molecular motion in the system. In the subtraction of the cured, postcured sample from the cured sample resonances are observed at 40.1, 36.4, 16.1 and 14.0 ppm. The resonances of the natural rubber carbons did not subtract out completely because of resonance broadening that occurs upon curing. The intensity increase of the peaks appearing at 40.1 and 16.1 ppm indicate additional cis-to-trans chain isomerization has occurred with postcuring. The resonance which appears at 36.4 ppm may indicate the appearance of cyclic sulfide structures in the vulcanizate. Cyclic sulfides were observed in the sulfur-vulcanized natural rubber of the previous study.

Natural rubber was formulated with the CBS accelerator under very specific conditions in order to generate a network system containing predominantly monosulfidic crosslinks. The resulting C-13 MAS/GHPD NMR spectrum of Figure 5-22(a) does not show any significant spectral changes. The crosslink density of the system was

apparently too low for the level of sensitivity in these NMR experiments which is on the order of 1%. Resonances due to monosulfidic crosslinks would be expected at roughly 50 ppm for structure D and at approximately 42 ppm for structure C of Table 5-7. The aliphatic carbon region shows indications of a small amount of cis-to-trans chain isomerization with the appearance of peaks at 40 and 16 ppm (much less than 1%). The new resonance peaks found in the NMR spectrum of the natural rubber-cured with MOR correspond to the same new resonances of the 10% TMTD system and also the LS02-TMTD10 system. These spectral observations generally indicate that similar network structures are obtained for these accelerated sulfur-cured natural rubber systems.

5.6.4. Motional Effects on Vulcanized Natural Rubber. Resonance broadening of the peaks due to the natural rubber carbons is observed for all the vulcanizate systems. This phenomenon has been observed in the past for crosslinked systems. Schaefer observed that the linewidths in the NMR spectra of polyisoprene systems were affected by crosslinking and the addition of carbon black. He also determined the spin-lattice relaxation times for the five different carbons and observed essentially no changes as a result of the crosslinking. The same results were found in this study. T_1 values were also determined for the peaks which appear at 57.5 and 44.6 ppm for the LS02-TMTD02 and LS02-TMTD10 systems. The spin-lattice relaxation times were found to correspond with the spin-lattice relaxation times of the sulfur systems studied previously. This is further evidence that the peaks which appear at 57.5 and 44.6 ppm in the C-13 NMR spectra of the vulcanizates obtained with different formulations are due to the same structural feature. In both cases the peaks are due to carbon-sulfur bonds which are part of the polysulfidic crosslinks. When accelerators are used, these resonances are also due to polysulfides terminated by accelerator residues.

The NMR spectra for this study were obtained for the most part by the gated high-power decoupling pulse sequence. This single-carbon pulse experiment is used for systems that are sufficiently mobile. Cross polarization was not used successfully for the systems considered above because of the lack of rigidity in these relatively lightly crosslinked vulcanizates. In the previous study, high levels of sulfur were used as the primary curing agent. The resulting rigidity and lack of molecular motion in the vulcanizates allowed for more effective use of the CP process. Komoroski studied a series of filled vulcanizates by MAS C-13 NMR spectroscopy. Using the GHPD technique with Bloch decays, and the cross polarization technique on the same set of samples, he determined that the Bloch decays provided the more accurate quantitative results. The conclusions were based on the fact that elastomers have

a considerable amount of chain mobility which makes the process of cross polarization inefficient. The necessary static dipolar interactions which facilitate the CP process in a sample are reduced by chain mobility.

In summary, the solid state C-13 NMR technique has proven to be a significant method for the detection of crosslinks and other structural modifications in sulfur-vulcanized natural rubber systems. The use of sulfur as a crosslinking agent by itself generates a considerable amount of main chain structural modifications. Cyclic sulfide structures and cis-to-trans chain isomerization are detected in addition to polysulfidic crosslinks which are found attached to different carbons of the natural rubber repeat unit. The phenomenon of reversion has also been detected in this study. The nature of the spectral broadening in the NMR spectra of the highly cured vulcanizates has two origins. The broadening arises from lack of molecular motion in the system and from an increase in chemical shift dispersion due to the new structures formed with crosslinking.

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